



Additivity methods for prediction of thermochemical properties. The Laidler method revisited. 2. Hydrocarbons including substituted cyclic compounds

Rui C. Santos^a, João P. Leal^{a,b,*}, José A. Martinho Simões^{a,c}

^a Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal

^b Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal

^c Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal

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ABSTRACT

A revised parameterization of the extended Laidler method for predicting standard molar enthalpies of atomization and standard molar enthalpies of formation at $T = 298.15$ K for several families of hydrocarbons (alkanes, alkenes, alkynes, polyenes, poly-yenes, cycloalkanes, substituted cycloalkanes, cycloalkenes, substituted cycloalkenes, benzene derivatives, and bi and polyphenyls) is presented. Data for a total of 265 gas-phase and 242 liquid-phase compounds were used for the calculation of the parameters. Comparison of the experimental values with those obtained using the additive scheme led to an average absolute difference of $0.73 \text{ kJ} \cdot \text{mol}^{-1}$ for the gas-phase standard molar enthalpy of formation and $0.79 \text{ kJ} \cdot \text{mol}^{-1}$ for the liquid-phase standard molar enthalpy of formation. The database used to establish the parameters was carefully reviewed by using, whenever possible, the original publications. A worksheet to simplify the calculation of standard molar enthalpies of formation and standard molar enthalpies of atomization at $T = 298.15$ K based on the extended Laidler parameters defined in this paper is provided as supplementary material.

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1. Introduction

Experimental values of standard enthalpies of formation are known for a tiny and decreasing fraction of the substances recorded by Chemical Abstracts, hindering the thermochemical assessment of many important chemical reactions. Although computational chemistry methods may afford accurate reaction enthalpies and enthalpies of formation, simple and inexpensive empirical routines will still be used at least in the next decades. Therefore, the development of more reliable procedures to predict those data is essential.

Additivity methods for estimating thermochemical properties have been widely used [1–19]. The main advantages of these methods when compared with other approaches, such as high-level theoretical calculations, is that they are simple to apply, do not require significant computing power, and usually provide very reliable values. However, the prediction of accurate data often demands a large number of empirical “parameters”, which in turn require many experimental values of the property to be parameterized. This is indeed the major disadvantage of additivity methods: their

empirical nature requires a reliable (experimental and/or computational) data collection.

In a previous paper one of us introduced an extended version of the Laidler method and applied it to a large number of hydrocarbons, stating also the intention to cover other families of compounds in future publications [17]. Most, but not all, of the work done relied on several databases, mainly Pedley’s compilation [13]. However, it was found later that some values from that database and also from NIST Chemistry WebBook [20] were not properly assigned. It was therefore decided to evaluate, whenever possible, all the experimental values, based on the original papers. On the other hand, a substantial increase in the database allowed calculating additional parameters, particularly for cyclic compounds. Also, some parameters were redefined and new ones added, including more non-bonded interactions, which allowed coverage of rather bulky compounds. Finally, in cases where conflicting experimental data exist, high-level theoretical calculations were performed to clarify the situation, *i.e.* to help selecting the “best” experimental value.

The results of this evaluation work, which are reported in the present paper, pave the ground to extend the model to other families of molecules, including compounds with heteroatoms.

The standard molar enthalpy of formation ($\Delta_f H_m^\circ$) is a key property because it reflects the enthalpic content of a molecule. It also allows calculating the enthalpy of any reaction where that molecule is involved, provided that the enthalpies of formation of all

* Corresponding author. Address: Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, 1749-016 Lisboa, Portugal. Tel.: +351 219946219.

E-mail addresses: jpleal@fc.ul.pt, jpleal@itn.pt (J.P. Leal).

the remaining compounds that participate in the reaction are known. Another useful quantity is the standard molar enthalpy of atomization ($\Delta_{\text{at}}H_{\text{m}}^{\circ}$), i.e. the enthalpy required to break all the chemical bonds in a given gas-phase molecule (reaction (1)). The enthalpy of atomization can therefore be understood as a sum of all the “bond enthalpies” in the molecule.



Several additivity methods have been developed to predict enthalpies of formation and atomization [1–4,6,10,13–15,17–19]. The most frequently used is the so-called Benson group method, which was proposed in 1958 by Benson and Buss [2a]. The parameters of Benson method have been refined and extended by several authors [2b,10]. Another method (or “scheme”) that is simple to use and very attractive to chemists, since it deals with bond enthalpies, is the Laidler method [1]. In this method the main parameters are assigned to the chemical bonds, and therefore should reflect the strengths of those bonds. In addition, the parameters can in principle be related to other properties, such as bond lengths. In the original formulation, for alkanes, Laidler defined one parameter for the C–C bond and three parameters for C–H bonds (primary, secondary, and tertiary carbon atoms). When the Laidler method was proposed, in 1956, it was important to keep the number of parameter as low as possible to minimize the calculation time. However, this is not a limitation today and some schemes use as many as 20 parameters for alkanes [13].

The Laidler method has been refined by Tatevski and coworkers [4] but only for alkanes. As mentioned above, another expansion of the Laidler method, involving a variety of hydrocarbon families, was reported by one of us [17]. In the present paper a parameterization of the Laidler method is proposed for gas- and liquid-phase standard molar enthalpies of formation and standard molar enthalpies of atomization at $T = 298.15$ K for alkanes, alkenes, alkynes, polyenes, polyynes, cycloalkanes, substituted cycloalkanes, cycloalkenes, substituted cycloalkenes, benzene derivatives, and bi and polyphenyls. This new parameterization improves the reliability of estimates (even for very large and bulky compounds) and extends the previous one to new families of hydrocarbon compounds. For future reference, the approach used in this paper will be called the Extended Laidler Bond Additivity (ELBA) Method.

We finally note that we are aiming at a high accuracy estimation method. Therefore, in some cases we have to increase the complexity (i.e. the number of parameters) or to introduce some purely empirical correction to keep the accuracy at the desired level. This choice will obviously make the use of our method more difficult. However, it is our goal to implement a user-friendly interface where the estimate will be done simply by drawing a molecular structure. This paper represents a first step for this final objective.

2. The ELBA method

The basic guideline for developing the ELBA method was that the accuracy of the prediction should not be compromised by imposing a limit to the number of parameters but the physical meaning of these parameters should be as clear as possible and easy to identify. Regarding the optimization procedure, it was decided that after the addition of any new family to the database all the parameters should be reoptimized. The multiparameter regression analysis was made using the Microsoft® Office Excel 2003 SP3 Solver Tool. The estimates were made by the tangent method and forward derivatives with Newton search. The values obtained in a previous paper were used as the initial guesses of the parameters [17].

For each compound the gas- and liquid-phase standard molar enthalpies of formation and the standard molar enthalpy of atomization were expressed as a sum of the parameters depending on the bond types and non-bonded interactions involved. For each one of those three quantities a specific set of parameters was defined. The description of many of these parameters was reported before [17] and will not be repeated here.

2.1. Alkanes, alkenes, and alkynes

For these families of compounds no change was introduced in the parameter list previously defined [17], with exception of the new parameter Z15 (figure 1), which takes into account steric hindrance in very bulky alkanes. For the sake of clarity, we recall that four different types of carbon atoms were considered (carbon atoms bonded to one, two, three or four carbons) in the parameterization of the alkanes, thus defining 10 different C–C bond types (from C1C1 to C4C4) and four different C–H bond types (C0H to C3H). For alkenes, three different sp^2 carbon atoms types were considered, leading to six distinct C=C bond types (D1D1 to D3D3), eight C–C bonds involving an sp^2 carbon (C1D2 to C4D3) and two sp^2 CH bonds (D1H and D2H). In addition, three non-bonded interactions (Z11, Z14, and Z44) were considered. For alkynes, two different types of carbon atoms were assumed, leading to three C≡C bonds (T1T1, T1T2, and T2T2), four C–C bonds involving an sp carbon (C1T2 to C4T2), and one C–H bond (T1H).

All the above parameters (22 C–C, 6 C=C, 3 C≡C, 7 C–H bonds, and 4 non-bonded parameters) were compiled in table 1.

2.2. Allenes, dienes, polyenes, diynes, and alkenynes

For these families of compounds no change was introduced in the parameter list previously defined [17]. To summarize, and considering the parameters of table 1, the only new type of carbon needed for the parameterization of allenes is the one that sits in the middle of two double bonds, leading to four new types of bonds (D1Dd, D2Dd, D3Dd, and DdDd). For dienes and polyenes, new parameters will be needed only in the case of conjugated double bonds (C–C bonds between two double bonds): Cd2Cd2, Cd2Cd3,

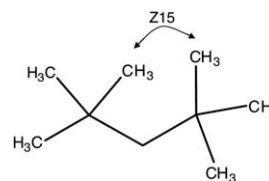


FIGURE 1. The Z15 parameter for alkanes.

TABLE 1

The Laidler parameters for alkanes, alkenes, and alkynes.

C–C bonds	C=C bonds	C≡C bonds	C–C bonds with an sp^2 carbon	C–C bonds with an sp carbon	C–H bonds	Non-bonded parameters
C1C1	D1D1	T1T1	C1D2	C1T2	C0H	Z11
C1C2	D1D2	T1T2	C1D3	C2T2	C1H	Z14
C1C3	D1D3	T2T2	C2D2	C3T2	C2H	Z44
C1C4	D2D2		C2D3	C4T2	C3H	Z15
C2C2	D2D3		C3D2		D1H	
C2C3	D3D3		C3D3		D2H	
C2C4			C4D2		T1H	
C3C3			C4D3			
C3C4						
C4C4						

TABLE 2

Laidler parameters for allenes, dienes, polyenes, diynes, and alkenynes.

C=C adjacent bonds	C–C bonds between two C=C bonds	C–C bonds between C=C and C≡C bonds	C–C bonds between two C≡C bonds
D1Dd	Cd2Cd2	Cd2Ct2	Ct2Ct2
D2Dd	Cd2Cd3	Cd3Ct2	
D3Dd	Cd3Cd3		
DdDd			

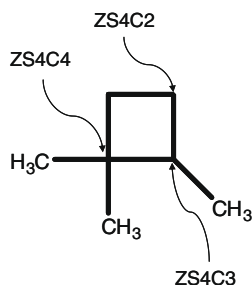
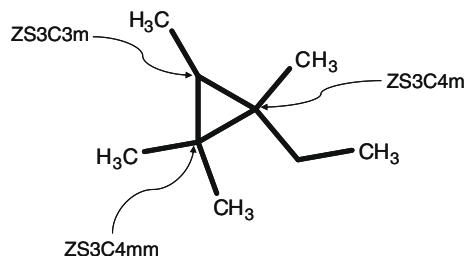
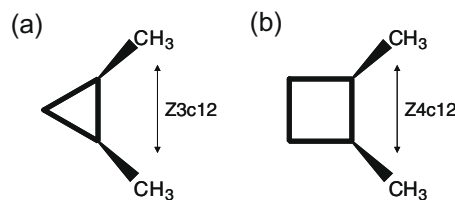
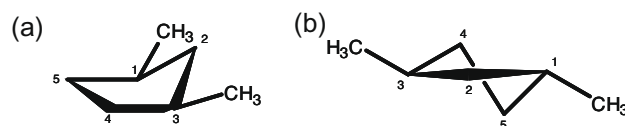
and Cd3Cd3. For diynes and alkenynes, there is the possibility of a single bond between two triple bonds (Ct2Ct2) or between a triple and a double bond (Cd2Ct2 and Cd3Ct2). All these parameters are compiled in table 2.

2.3. Cycloalkanes and cycloalkenes

For cycloalkanes and cycloalkenes a drastic change in parameter definition was made. Several ring strain parameters were used in reference [17], a set of them for cycloalkanes and another one for cycloalkenes, both depending on the size of the ring. A completely different approach was followed in this work: instead of considering a strain parameter for each ring, a strain parameter is defined for each atom of the ring. At first sight, this difference may not seem relevant, but it allows a simpler expansion of the method to substituted cyclic compounds and, in the future, with the introduction of heteroatoms in the ring, the new approach will be rather important.

Three strain parameters were considered for cycloalkanes, according to the fact that the carbon atom in the ring can be secondary, tertiary or quaternary (ZSnC2, ZSnC3, and ZSnC4, n = size of the ring) (figure 2). A new strain parameter (ZSnD3, n = size of the ring) is also introduced for up to six-atom rings, to be considered when a double bond is connected directly to the ring.

In addition to those general parameters, new corrective parameters must be introduced in some cases. For example, it was found that in the case of three-atom ring compounds the strain produced by one methyl group is different from the strain produced by higher alkyls. It was also noted that one or two methyl groups bonded

**FIGURE 2.** Atomic strain parameters for cycloalkanes, illustrated for a cyclobutane.**FIGURE 3.** Non-bonded parameters for cyclopropanes.**FIGURE 4.** Two examples of the Znc12 interaction: (a) Z3c12 and (b) Z4c12.**FIGURE 5.** The most stable conformational arrangements of the 1,3-dimethylcyclopentane isomers. (a) *cis* isomer in a 1,3-diequatorial envelope conformation and (b) *trans* isomer in a 1,3-diequatorial half-chair conformation.

to the same ring atom produce different strain. Therefore, three new strain parameters were defined (ZS3C3m, ZS3C4m, and ZS3C4mm) for this family of compounds (figure 3).

In small rings (three to six atoms) it was found that some additional non-bonded parameters were required to account for interactions between ring substituents. For three- to five-atom rings there is a non-bonded interaction between *cis*-1,2-substituents (Znc12, n = 3 to 5) (figure 4). Also, in five-atom rings with 1,3-substituents, an additional non-bonded interaction exists in one of the *cis*–*trans* isomers. For the *cis* isomer, the most stable arrangement is an envelope conformation (see example in figure 5a) with the 1,3-substituents in the equatorial positions (numbered as in figure 5a). When the substituents change to a *trans* arrangement, as in the case of *trans*-1,3-dimethylcyclopentane, the most stable conformation forces the ring to assume an half-chair arrangement (figure 5b) with the two 1,3-substituents in the equatorial positions (numbered as in figure 5b). An extra parameter (Z5t13) had to be defined for this last case. In six-atom rings with only one substituent, the molecule will preferentially assume a conformation with that substituent in an equatorial position, but with two substituents in *cis*-1,2, *trans*-1,3, or *cis*-1,4 positions it is not possible to avoid one of them to be in axial position. The presence of at least one substituent in axial position in six-atom rings produces a

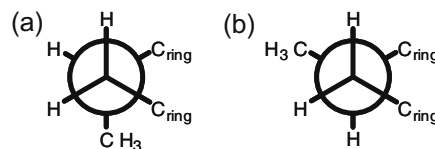
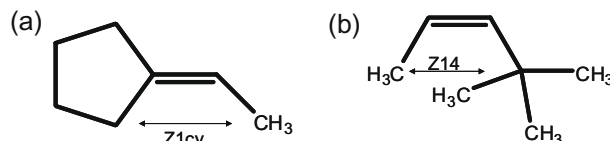
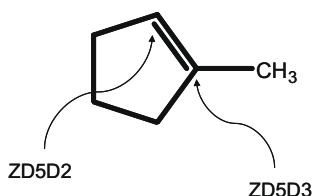
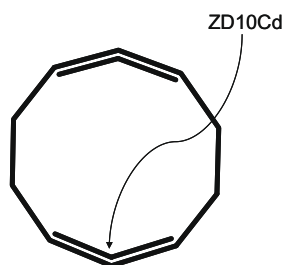
**FIGURE 6.** There are three situations where a six-atom ring with two substituents is forced to have at least one of them in the axial position: *cis*-1,2, *trans*-1,3, and *cis*-1,4. The fact that one of them is in the axial position (a), yields an extra non-bonded interaction when compared with a substituent in an equatorial position (b).**FIGURE 7.** (a) Interaction between a ring and other substituent in a double bond. (b) Interaction between substituents in a double bond not involving a ring.

TABLE 3

Strain and non-bonded parameters for cycloalkanes.

3-atom ring	4-atom ring	5-atom ring	6-atom ring	<i>n</i> - (7 to 17) atom ring ^a	10-atom ring
ZS3C2	ZS4C2	ZS5C2	ZS6C2	ZSnC2	Z10int
ZS3C3	ZS4C3	ZS5C3	ZS6C3	ZSnC3	
ZS3C3m	ZS4C4	ZS5C4	ZS6C4	ZSnC4	
ZS3C4	ZS4D3	ZS5D3	ZS6D3		
ZS3C4m	Z4c12	Z5c12	Z6ax		
ZS3C4mm		Z5t13			
ZS3D3					
Z3c12					

^a ZSnD3 parameter for $n \geq 7$ is not given because there are no experimental values for a compound with a double bond connected to a $n \geq 7$ ring.

**FIGURE 8.** General strain parameters for cycloalkenes: example for a five-atom ring.**FIGURE 9.** The ZD10Cd strain parameter defined for a 10-atom ring compound containing two consecutive double bonds.

destabilizing interaction between those substituents and the ring carbon atoms (Z6ax) (figure 6). Also, with 1,3,5-substituents the α, α, α isomer has the more stable conformation with all the substituents in an equatorial position, but in the α, α, β isomer it is not possible to avoid one of the substituents to be in axial position.

In the cases of a double bond connected to a ring, a non-bonded interaction could exist between the substituents of the double bond, like in any other alkene. This interaction is, however, different from the cases of single alkyl substituents and therefore a new parameter (Z1cy) was introduced (figure 7).

In the stable cyclodecane conformation, one may discern two kinds of C–H bonds: those that point out from the ring (extra-

annular) and those that point into the ring (intra-annular). Groups other than hydrogen in intra-annular positions would clearly be in a highly strained situation [21]. To take this problem into account, a non-bonded term (Z10int) was defined for the cases of disubstituted 10-atom rings in any of the 2, 3, 5, 7, 8 or 10 positions.

All strain and non-bonded parameters (with the exception of Z1cy, which is valid for rings of any dimension) defined for cycloalkanes are presented in table 3.

For cycloalkenes it was necessary to define several conformational parameters to take into account the distortion caused by the presence of one or more double bonds in the ring, in addition to the strain parameters with a similar meaning to those defined for cycloalkanes. The new parameters for cycloalkenes are represented by ZDnDm ($n = 3$ to 10, 12, and $m = 2, 3$, $n =$ size of the ring, and $m =$ number of atoms connected to the carbon atom under consideration) and ZD10Cd. An example of the first group of parameters is shown in figure 8 and the parameter ZD10Cd is illustrated in figure 9. For five-atom rings, when the ring is unsubstituted, independent of the number of double bonds, the system seems to have a high ability to find a more stable conformation and a supplementary parameter (Z5) was introduced to account for that. For six-atom rings having one or two double bonds, two additional parameters (Z6 and Z6s) were defined and used according to the compound structure. Reliable experimental data are scarce for compounds involving this type of unsaturated rings, affecting the correct parameterization. The parameter Z6s was needed as an additional correction to Z6 for molecules that have the isopropenyl substituent in their structure (e.g. (R)-1-methyl-4-(1-methylethenyl)cyclohexene). In the particular case of a six-atom unsubstituted ring, with two unconjugated double bonds (e.g., 1,4-cyclohexadiene), it was found that no correction is necessary. Once again due to the scarcity of experimental data, the corrections for this type of substituted unsaturated ring are unknown. For compounds with one double bond in the ring, the term Z6 is multiplied by two both in the absence and in the presence of one substituent (e.g. cyclohexene, 1-methylcyclohexene), or by four when two substituents are present (e.g. (R)-1-methyl-4-(1-methylethenyl)cyclohexene). If the compound has two conjugated double bonds in the ring, the term Z6 is multiplied by eight in the absence of substituents (e.g. 1,3-cyclohexadiene), or by five in the presence of one or two substituents (e.g. 2-methyl-1,3-cyclohexadiene, 5-isopropyl-2-methyl-1,3-cyclohexadiene).

Due to the several possible conformations of eight-atom rings having one or two double bonds, four new parameters become necessary. These rings can have the double bonds in (E) or (Z) conformations. For rings with only one double bond, when a (Z) conformation occurs no extra parameter is needed but for an (E) conformation the Z8uE parameter must be used. In the case of two double bonds in the ring, a total of three combinations are possible, which will be described by the parameters Z8uEE, Z8uZZ, and Z8uZE.

When rings have three or four double bonds, the conformational correction used is described by the parameter ZnuABCD,

TABLE 4

Strain and conformational parameters for cycloalkenes.

<i>n</i> - (3 and 4) atom ring	5-atom ring	6-atom ring	7-atom ring	8-atom ring	9-atom ring	10-atom ring	12-atom ring
ZDnD2	ZD5D2	ZD6D2	ZD7D2	ZD8D2	ZD9D2	ZD10D2	ZD12D2
ZDnD3	ZD5D3	ZD6D3	ZD7D3	ZD8D3	ZD9D3	ZD10D3	ZD12D3
	Z5	Z6	Z7u13	Z8uE		ZD10Cd	Z12u159E
		Z6s	Z7u135	Z8uEE		Z10u1267	
				Z8uZZ			
				Z8uZE			
				Z8u136			
				Z8u1357			

TABLE 5
Parameters for benzene derivatives.

Bonds in benzene ring	Alkyl groups bonded to the benzene ring	Non-alkyl groups bonded to the benzene ring	Non-bonded parameters (neighbours repulsion)		
A2A2	C1A3	D2A3	ZA11	ZA11'	ZA1'4'
A2A3	C2A3	D3A3	ZA14	ZA1'4	ZA4'1
A3A3	C3A3	T2A3	ZA44	ZA1'1'	ZA4'4'
A2H	C4A3				

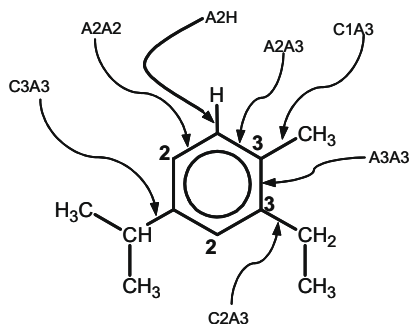


FIGURE 10. The two different types of carbons in a benzene ring (bold) and several carbon–carbon and carbon–hydrogen bond types.

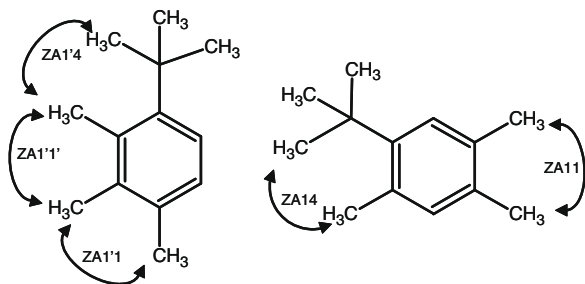


FIGURE 11. Additional bond types between a benzene ring and unsaturated substituents.

where $n = 7, 8$, or 10 is the size of the ring, and A, B, C , and D are the positions of the double bonds in the ring. A special case is the twelve-atom ring parameter Z12u159E, which is used when all the three double bonds in the ring are in (E) conformation.

The parameters proposed for cycloalkenes are presented in table 4.

2.4. Benzene derivatives

For benzene and its derivatives the parameters are as defined previously (table 5) [17]. For the sake of clarity, some examples are presented in figures 10 and 11.

2.5. Bi and polyphenyls

The only new parameter required to cover biphenyls is the one related to the bond between the aromatic rings, Ca3Ca3. However, two additional parameters were also defined to take in account the non-bonded interaction that occurs in some biphenyl and polyphenyl compounds. In biphenyls with a substituent in position 2, the repulsive interaction is described by the ZA1A parameter (figure 12). For polyphenyls, a stabilizing interaction ZAA was found when two aromatic rings are near each other, out of plane (figure 13).

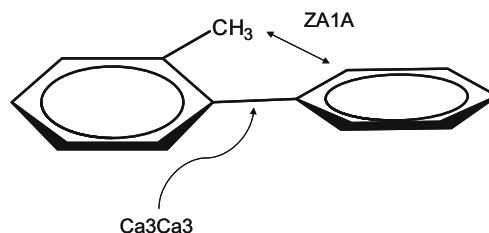


FIGURE 12. New bond and non-bonded parameters for biphenyls.

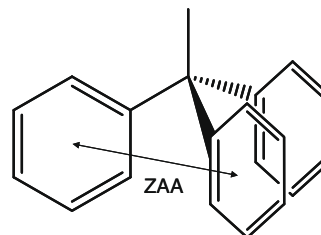


FIGURE 13. The interaction between two aromatic rings in polyphenyls.

3. Experimental values

As the proposed ELBA method is empirical, relying on a fitting procedure, the quality of the experimental database is crucial, *i.e.* the input values should be accurate and thermochemically consistent. By thermochemical consistency it is meant that all the standard enthalpies of formation calculated from experimental values of reaction or combustion enthalpies should rely on a single set of auxiliary data. For instance, suppose that the reported enthalpies of formation of compounds A and B, both obtained from highly accurate measurements of their combustion enthalpies, were reported by two different groups who had different choices for the values of the standard molar enthalpies of formation of water and carbon dioxide. In this case, the reported $\Delta_f H_m^\circ(A)$ will be “inconsistent” with $\Delta_f H_m^\circ(B)$ no matter how good the experimental measurements were. Although in the case of hydrocarbons this is not a serious problem, because $\Delta_f H_m^\circ(H_2O, g)$ and $\Delta_f H_m^\circ(CO_2, g)$ are well established, inconsistency appears when A and B have large numbers of carbon atoms and/or when the original literature reference is rather old. It is therefore important to recalculate all values using the same set of auxiliary data, in order to ensure consistency. The values of the standard molar enthalpies of formation at $T = 298.15$ K in table 6 were taken from the compilation made by Pedley [13], unless noted otherwise. When taken from other sources, the values were checked to see if they rely on the same set of auxiliary data as Pedley's. If not, they were recalculated from the original measurements, and rely on $\Delta_f H_m^\circ(H_2O, l) = -285.830 \pm 0.040 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\circ(CO_2, g) = -393.51 \pm 0.13 \text{ kJ} \cdot \text{mol}^{-1}$ [22]. The standard molar enthalpies of atomization were derived by using $\Delta_f H_m^\circ(H, g) = 217.999 \pm 0.006 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\circ(C, g) = 716.67 \pm 0.46 \text{ kJ} \cdot \text{mol}^{-1}$ [22].

4. Results

4.1. Parameters

The application of the procedure describe above to the data in table 6 (265 gas-phase standard molar enthalpies of formation, 242 liquid-phase standard molar enthalpies of formation, and

TABLE 6

Experimental and estimated values for hydrocarbons at $T = 298.15$ K. Data in $\text{kJ} \cdot \text{mol}^{-1}$.

Compound		Experimental gas-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase standard molar enthalpy of formation		Experimental liquid-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted liquid-phase standard molar enthalpy of formation		Experimental standard molar enthalpy of atomization ^b		Estimated value and difference between exp. and fitted standard molar enthalpy of atomization	
Formula	Name	Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
<i>Alkanes</i>													
CH ₄	Methane	−74.4	0.4	−74.4	0.0					1663.1	0.4	1663.1	0.0
C ₂ H ₆	Ethane	−83.8	0.3	−83.8	0.0	−93.6	2.5	−93.6	0.0	2825.1	0.3	2825.0	0.2
C ₃ H ₈	Propane	−104.7	0.5	−104.8	0.1	−120.9	2.5	−121.9	1.0	3998.7	0.5	3998.9	−0.2
C ₄ H ₁₀	Butane	−125.7	0.6	−125.6	−0.1	−147.3	2.5	−147.5	0.2	5172.4	0.6	5172.3	0.0
	2-Methylpropane	−134.2	0.6	−134.7	0.5	−154.2	1.2	−154.8	0.6	5180.9	0.6	5181.5	−0.6
C ₅ H ₁₂	Pentane	−146.9	0.8	−146.3	−0.6	−173.5	0.7	−173.1	−0.4	6346.2	0.8	6345.8	0.5
	2-Methylbutane	−153.6	0.9	−153.0	−0.6	−178.4	0.9	−178.1	−0.3	6352.9	0.9	6352.4	0.5
	2,2-Dimethylpropane	−168.0	0.8	−170.1	2.1	−190.2	0.7	−192.0	1.8	6367.3	0.8	6369.4	−2.1
C ₆ H ₁₄	Hexane	−166.9	0.8	−167.1	0.2	−198.7	0.8	−198.7	0.0	7518.9	0.8	7519.2	−0.3
	2-Methylpentane	−174.6	0.9	−173.8	−0.8	−204.6	0.9	−203.8	−0.8	7526.6	0.9	7525.8	0.8
	3-Methylpentane	−171.9	0.9	−171.3	−0.6	−202.4	0.9	−201.5	−0.9	7523.9	0.9	7523.4	0.5
	2,2-Dimethylbutane	−185.9	0.9	−184.7	−1.2	−213.8	0.9	−212.0	−1.8	7537.9	0.9	7536.7	1.2
	2,3-Dimethylbutane	−178.1	0.9	−176.1	−2.0	−207.4	0.9	−204.6	−2.8	7530.1	0.9	7528.1	2.0
C ₇ H ₁₆	Heptane	−187.6	1.3	−187.8	0.2	−224.2	1.3	−224.3	0.1	8692.3	1.3	8692.6	−0.3
	2-Methylhexane	−194.5	1.0	−194.5	0.0	−229.5	1.0	−229.4	−0.1	8699.2	1.0	8699.2	−0.1
	3-Methylhexane	−191.3	1.9	−192.1	0.8	−226.4	1.9	−227.1	0.7	8696.0	1.9	8696.8	−0.8
	3-Ethylpentane	−189.5	1.1	−189.6	0.1	−224.9	1.1	−224.8	−0.1	8694.2	1.1	8694.3	−0.1
	2,2-Dimethylpentane	−205.7	1.5	−205.5	−0.2	−238.3	1.5	−237.6	−0.7	8710.4	1.5	8710.1	0.2
	2,4-Dimethylpentane	−201.6	1.1	−201.2	−0.4	−234.6	1.1	−234.4	−0.2	8706.3	1.1	8705.9	0.4
	3,3-Dimethylpentane	−201.0	1.1	−199.3	−1.7	−234.2	1.1	−232.0	−2.2	8705.7	1.1	8704.0	1.7
	2,2,3-Trimethylbutane	−204.4	1.3	−203.0	−1.4	−236.5	1.3	−235.5	−1.0	8709.1	1.3	8707.7	1.4
	Octane	−208.5	1.3	−208.6	0.1	−250.1	1.3	−249.9	−0.2	9865.8	1.3	9866.0	−0.2
C ₈ H ₁₈	2-Methylheptane	−215.3	1.4	−215.3	0.0	−255.0	1.4	−255.0	0.0	9872.6	1.4	9872.6	0.0
	3-Methylheptane	−212.5	1.3	−212.8	0.3	−252.3	1.3	−252.7	0.4	9869.8	1.3	9870.2	−0.4
	4-Methylheptane	−211.9	1.3	−212.8	0.9	−251.6	1.3	−252.7	1.1	9869.2	1.3	9870.2	−1.0
	3-Ethylhexane	−210.7	1.3	−210.4	−0.3	−250.4	1.3	−250.4	0.0	9868.0	1.3	9867.7	0.3
	2,2-Dimethylhexane	−224.5	1.3	−226.2	1.7	−261.9	1.3	−263.2	1.3	9881.8	1.3	9883.5	−1.7
	2,3-Dimethylhexane	−213.8	1.6	−215.2	1.4	−252.6	1.6	−253.6	1.0	9871.1	1.6	9872.5	−1.3
	2,4-Dimethylhexane	−219.2	1.3	−219.5	0.3	−257.0	1.3	−257.7	0.7	9876.5	1.3	9876.8	−0.3
	2,5-Dimethylhexane	−222.5	1.6	−222.0	−0.5	−260.4	1.6	−260.0	−0.4	9879.8	1.6	9879.3	0.5
	3,3-Dimethylhexane	−219.9	1.3	−220.1	0.2	−257.5	1.3	−257.5	0.0	9877.2	1.3	9877.4	−0.2
	3,4-Dimethylhexane	−212.8	1.6	−212.7	−0.1	−251.8	1.6	−251.3	−0.5	9870.1	1.6	9870.0	0.1
	3-Ethyl-2-methylpentane	−211.0	1.4	−212.7	1.7	−249.6	1.4	−251.3	1.7	9868.3	1.4	9870.0	−1.7
	3-Ethyl-3-methylpentane	−214.8	1.4	−214.0	−0.8	−252.8	1.4	−252.0	−0.8	9872.1	1.4	9871.3	0.9
	2,2,3-Trimethylpentane	−219.9	1.6	−221.3	1.4	−256.9	1.6	−258.9	2.0	9877.2	1.6	9878.6	−1.4
	2,2,4-Trimethylpentane	−223.9	1.5	−224.5	0.6	−259.2	1.5	−259.7	0.5	9881.2	1.5	9881.8	−0.6
	2,3,3-Trimethylpentane	−216.2	1.5	−217.7	1.5	−253.5	1.5	−255.5	2.0	9873.5	1.5	9875.0	−1.4
	2,3,4-Trimethylpentane	−217.2	1.7	−217.5	0.3	−255.0	1.7	−254.4	−0.6	9874.5	1.7	9874.8	−0.2
	2,2,3,3-Tetramethylbutane	−226.0	1.4	−224.2	−1.8			−258.3		9883.3	1.4	9881.6	1.8
C ₉ H ₂₀	2,2,3,3-Tetramethylpentane	−237.1	1.5	−238.9	1.8	−278.3	1.5	−278.3	0.0	11047.1	1.5	11048.9	−1.8
	2,2,3,4-Tetramethylpentane	−236.9	1.3	−236.0	−0.9	−277.7	1.2	−276.8	−0.9	11046.9	1.3	11046.0	0.9
	2,3,3,4-Tetramethylpentane	−236.1	1.7	−236.0	−0.1	−277.9	1.6	−279.1	1.2	11046.1	1.7	11046.0	0.2
C ₁₁ H ₂₄	3,3,5,5-Tetramethylheptane	−276.7	3.0	−277.0	0.3	−325.7	2.9	−324.9	−0.8	13392.0	3.0	13392.4	−0.3
	2,2,4,4,5-Pentamethylhexane	−281.0	3.0	−280.7	−0.3	−329.0	2.9	−328.5	−0.5	13396.3	3.0	13396.1	0.3
C ₁₅ H ₃₂	4,6-Diethyl-4,6-dimethylnonane	−347.1	4.2	−347.8	0.7	−414.7	4.2	−416.2	1.5	18073.1	4.2	18073.8	−0.6

(continued on next page)

TABLE 6 (continued)

Compound		Experimental gas-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase standard molar enthalpy of formation		Experimental liquid-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted liquid-phase standard molar enthalpy of formation		Experimental standard molar enthalpy of atomization ^b		Estimated value and difference between exp. and fitted standard molar enthalpy of atomization	
Formula	Name	Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
<i>Alkenes</i>													
C ₂ H ₄	Ethene	52.5	0.3	52.5	0.0					2252.8	0.3	2252.9	0.0
C ₃ H ₆	Propene	20.0	0.7	20.3	−0.3	4.0	2.5	3.3	0.7	3438.0	0.7	3437.7	0.3
C ₄ H ₈	1-Butene	0.1	0.9	0.1	0.0	−20.8	1.0	−20.8	0.0	4610.6	0.9	4610.3	0.2
	(Z)-2-Butene	−7.1	1.0	−7.8	0.7	−29.8	1.0	−30.6	0.8	4617.8	1.0	4618.4	−0.7
	(E)-2-Butene	−11.4	1.0	−11.9	0.5	−33.3	1.1	−34.0	0.7	4622.1	1.0	4622.6	−0.5
	2-Methylpropene	−16.9	0.9	−16.4	−0.5	−37.5	0.9	−37.8	0.3	4627.6	0.9	4627.2	0.4
C ₅ H ₁₀	1-Pentene	−21.1	0.9	−21.0	−0.1	−46.9	0.7	−47.2	0.3	5784.4	0.9	5784.4	0.0
	(Z)-2-Pentene	−27.6	0.9	−28.4	0.8	−53.7	0.7	−55.5	1.8	5790.9	0.9	5791.7	−0.8
	(E)-2-Pentene	−31.9	1.0	−32.5	0.6	−58.2	0.8	−58.8	0.6	5795.2	1.0	5795.9	−0.6
	2-Methyl-1-butene	−35.2	0.9	−36.5	1.3	−61.1	0.8	−62.1	1.0	5798.5	0.9	5799.8	−1.3
	3-Methyl-1-butene	−27.5	0.7	−28.8	1.3	−51.5	0.6	−52.6	1.1	5790.8	0.7	5792.2	−1.3
	2-Methyl-2-butene	−41.7	1.0	−41.0	−0.7	−68.6	1.1	−68.2	−0.4	5805.0	1.0	5804.4	0.6
C ₆ H ₁₂	1-Hexene	−43.5	1.6	−41.8	−1.7	−74.2	1.6	−72.8	−1.4	6959.5	1.6	6957.9	1.7
	(E)-2-Hexene	−53.9	1.5	−53.2	−0.7	−85.5	1.5	−84.4	−1.1	6969.9	1.5	6969.3	0.6
	(Z)-3-Hexene	−47.6	1.3	−49.0	1.4	−78.9	1.3	−80.3	1.4	6963.6	1.3	6965.0	−1.4
	(E)-3-Hexene	−54.4	1.3	−53.1	−1.3	−86.1	1.3	−83.7	−2.4	6970.4	1.3	6969.1	1.3
	2-Methyl-1-pentene	−59.4	1.3	−57.3	−2.1	−90.0	1.3	−87.7	−2.3	6975.4	1.3	6973.2	2.2
	3-Methyl-1-pentene	−49.5	1.5	−47.1	−2.4	−78.2	1.5	−75.9	−2.3	6965.5	1.5	6963.1	2.4
	4-Methyl-1-pentene	−51.3	1.8	−48.5	−2.8	−80.0	1.8	−77.8	−2.2	6967.3	1.8	6964.5	2.8
	(Z)-3-Methyl-2-pentene	−62.3	1.4	−61.1	−1.2	−94.5	1.4	−92.6	−1.9	6978.3	1.4	6977.0	1.3
	(E)-3-Methyl-2-pentene	−63.1	1.3	−61.1	−2.0	−94.6	1.3	−92.6	−2.0	6979.1	1.3	6977.0	2.1
	(Z)-4-Methyl-2-pentene	−57.5	1.1	−56.9	−0.6	−87.0	1.1	−86.5	−0.5	6973.5	1.1	6972.9	0.6
	(E)-4-Methyl-2-pentene	−61.5	1.4	−61.0	−0.5	−91.6	1.4	−89.9	−1.7	6977.5	1.4	6977.0	0.5
	2-Ethyl-1-butene	−56.0	1.4	−56.6	0.6	−87.1	1.4	−86.5	−0.6	6972.0	1.4	6972.4	−0.4
	2,3-Dimethyl-1-butene	−62.4	1.3	−60.9	−1.5	−93.2	1.9	−91.9	−1.3	6978.4	1.3	6977.0	1.4
	2,3-Dimethyl-2-butene	−68.1	1.1	−68.6	0.5	−101.4	1.3	−102.3	0.9	6984.1	1.1	6984.7	−0.6
C ₇ H ₁₄	1-Heptene	−62.3	0.9	−62.6	0.3	−97.9	0.9	−98.4	0.5	8131.0	0.9	8131.3	−0.3
	(Z)-2-Heptene			−69.9		−105.1	0.8	−106.7	1.6			8138.5	
	(E)-2-Heptene			−74.0		−109.5	0.8	−110.0	0.5			8142.7	
	(Z)-3-Heptene			−76.1		−104.3	0.7	−105.1	0.8			8497.3	
	(E)-3-Heptene			−80.2		−109.3	1.0	−108.5	−0.8			8501.4	
	(Z)-3-Methyl-3-hexene	−79.4	1.1	−81.7	2.3	−115.9	1.1	−117.4	1.5	8148.1	1.1	8150.3	−2.2
	2,4-Dimethyl-1-pentene	−83.8	1.3	−84.7	0.9	−117.0	1.3	−118.4	1.4	8152.5	1.3	8153.3	−0.8
	4,4-Dimethyl-1-pentene	−81.6	1.9	−80.2	−1.4	−110.6	1.8	−111.6	1.0	8150.3	1.9	8148.8	1.5
	(Z)-4,4-Dimethyl-2-pentene	−72.6	1.4	−72.6	0.0	−105.3	1.4	−105.3	0.0	8141.3	1.4	8141.3	0.0
	(E)-4,4-Dimethyl-2-pentene	−88.8	1.1	−88.7	−0.1	−121.7	1.1	−120.9	−0.8	8157.5	1.1	8157.4	0.1
	2,4-Dimethyl-2-pentene	−88.7	1.1	−90.1	1.4	−123.1	1.1	−124.1	1.0	8157.4	1.1	8158.9	−1.5
	2-Ethyl-3-methyl-1-butene	−79.5	1.4	−81.0	1.5	−114.1	1.4	−116.2	2.1	8148.2	1.4	8149.6	−1.4
	2,3,3-Trimethyl-1-butene	−85.5	1.3	−85.5	0.0	−117.7	1.3	−117.7	0.0	8154.2	1.3	8154.2	0.0
C ₁₀ H ₂₀	(Z)-2,2,5,5-Tetramethyl-3-hexene	−127.0 ^c		−127.0	0.0	−163.6	1.9	−163.6	0.0	11653.7		11653.7	0.0
	(E)-2,2,5,5-Tetramethyl-3-hexene	−165.5	2.6	−165.5	0.0	−207.5	2.6	−207.9	0.4	11692.2	2.6	11692.1	0.0
<i>Alkynes</i>													
C ₂ H ₂	Ethyne	226.7 ^d	0.8	226.7	0.0	208.7 ^e	5	208.7	0.0	1642.6	0.8	1642.6	0.0
C ₃ H ₄	Propyne	185.4 ^d	0.9	186.7	−1.3			166.5		2836.6	0.9	2835.3	1.3
C ₄ H ₆	1-Butyne	165.2 ^f	0.9	165.7	−0.5	141.4	1.3	141.0	0.4	4009.5	0.9	4008.9	0.5
	2-Butyne	145.1 ^f	1.0	146.2	−1.1	119.1	1.1	120.3	−1.2	4029.6	1.0	4028.4	1.1

C ₅ H ₈	1-Pentyne	144.3 ^d	2.1	145.0	−0.7			115.4		5183.0	2.1	5182.4	0.7
	2-Pentyne	128.9 ^d	2.1	125.2	3.7			94.9		5198.4	2.1	5202.1	−3.7
	3-Methyl-1-butyne	136.4 ^d	2.1	136.4	0.0	109.1 ^e	5	109.1	0.0	5190.9	2.1	5191.1	−0.2
C ₆ H ₁₀	1-Hexyne	122.3 ^g	1.2	124.2	−1.9			89.8		6357.7	1.2	6355.8	1.9
	2-Hexyne	107.7 ^g	2.4	104.5	3.2			69.3		6372.3	2.4	6375.5	−3.2
	3-Hexyne	105.4 ^g	1.9	104.3	1.1			69.4		6374.6	1.9	6375.8	−1.2
	3,3-Dimethyl-1-butyne	107.0 ^h	1.3	107.0	0.0	77.9 ⁱ	1.5	77.7	0.2	6373.0	1.3	6373.0	0.0
C ₇ H ₁₂	1-Heptyne	103.8 ^g	2.6	103.4	0.4	62.8 ^j		64.2	−1.4	7528.9	2.6	7529.2	−0.3
	2-Heptyne	84.8 ^g	2.2	83.7	1.1			43.7		7547.9	2.2	7548.9	−1.1
	3-Heptyne	82.8 ^g	2.4	83.5	−0.7			43.8		7549.9	2.4	7549.2	0.7
C ₈ H ₁₄	1-Octyne	80.7 ^g	3.6	82.7	−2.0	38.4 ^e	3.6	38.6	−0.2	8704.6	3.6	8702.6	2.0
	2-Octyne	63.8 ^g	1.5	63.0	0.8	19.3 ^e	1.5	18.1	1.2	8721.5	1.5	8722.4	−0.8
	3-Octyne	62.5 ^g	1.8	62.7	−0.2	18.6 ^e	1.8	18.2	0.4	8722.8	1.8	8722.6	0.2
	4-Octyne	60.1 ^g	2.1	62.7	−2.6	17.3 ^e	2.1	18.2	−0.9	8725.2	2.1	8722.6	2.6
C ₉ H ₁₆	1-Nonyne	62.3 ^g	3.0	61.9	0.4			13.0		9875.7	3.0	9876.0	−0.3
	2-Nonyne	42.6 ^g	3.0	42.2	0.4			−7.5		9895.4	3.0	9895.8	−0.4
	3-Nonyne	42.0 ^g	2.5	42.0	0.0			−7.4		9896.0	2.5	9896.0	0.0
	4-Nonyne	42.0 ^g	2.8	42.0	0.0			−7.4		9896.0	2.8	9896.0	0.0
<i>Allenes, dienes, polyenes</i>													
C ₃ H ₄	Propadiene	190.5	1.1	190.9	−0.4			41.9		2831.5	1.1	2831.1	0.4
C ₄ H ₆	1,2-Butadiene	162.3	0.6	162.2	0.1	139.0	0.6	139.0	0.0	4012.4	0.6	4012.5	−0.1
	1,3-Butadiene	110.0	1.1	108.6	1.4	88.5	1.2	88.6	−0.1	4064.7	1.1	4066.2	−1.5
C ₅ H ₈	1,2-Pentadiene	140.7	0.7	141.6	−0.9			114.1		5186.6	0.7	5185.8	0.9
	(Z)-1,3-Pentadiene	81.4	1.2	80.5	0.9			54.7		5245.9	1.2	5246.8	−0.9
	(E)-1,3-Pentadiene	76.1	0.8	76.4	−0.3			51.3		5251.2	0.8	5251.0	0.3
	1,4-Pentadiene	105.7	1.1	104.2	1.5			78.8		5221.6	1.1	5223.1	−1.5
	2,3-Pentadiene	133.1	0.8	133.5	−0.4			236.1		5194.2	0.8	5193.8	0.4
	3-Methyl-1,2-butadiene	129.1 ^k	0.6	129.1	0.0	101.2	0.5	101.2	0.0	5198.3	0.6	5198.2	0.1
	2-Methyl-1,3-butadiene	75.5	1.1	74.2	1.3	48.2	1.3	48.6	−0.4	5251.8	1.1	5253.1	−1.3
C ₆ H ₈	(Z)-2,3,4-Hexatriene	265 ^l		265.0	0.0			236.1		5779.0		5779.0	0.0
	(E)-2,3,4-Hexatriene	265 ^l		265.0	0.0			236.1		5779.0		5779.0	0.0
C ₆ H ₁₀	1,5-Hexadiene	84.2	0.9	83.5	0.7	54.1	0.4	53.2	0.9	6395.8	0.9	6396.5	−0.7
	(Z)-1,3-Hexadiene	59.0 ^m	2.0	59.9	−0.9			29.8		6421.0	2.0	6420.1	0.9
	(E)-1,3-Hexadiene	54.0 ^m	2.0	55.8	−1.8			26.5		6426.0	2.0	6424.3	1.7
	(Z)-1,4-Hexadiene	77.0 ^m	2.0	76.2	0.8			44.9		6403.0	2.0	6403.8	−0.8
	(E)-1,4-Hexadiene	74.0 ^m	2.0	72.0	2.0			41.5		6406.0	2.0	6408.0	−1.9
	(Z,Z)-2,4-Hexadiene	52.0 ^m	2.0	52.4	−0.4			20.8		6428.0	2.0	6427.5	0.5
	(E,Z)-2,4-Hexadiene	48.0 ^m	2.0	48.3	−0.3			17.4		6432.0	2.0	6431.7	0.3
	(E,E)-2,4-Hexadiene	44.0 ^m	2.0	44.2	−0.2			14.1		6436.0	2.0	6435.8	0.2
	2,3-Dimethyl-1,3-butadiene	45.3	1.1	45.5	−0.2	14.4	1.2	14.4	0.0	6434.7	1.1	6434.4	0.4
C ₈ H ₁₀	1,2,6,7-Octatetraene	369 ⁿ		367.3	1.7			324.6		7544.4		7546.0	−1.7
C ₈ H ₁₂	(E)-2,5-Dimethyl-1,3,5-hexatriene	95.8 ^l		96.0	−0.2			56.7		8253.5		8253.3	0.2
	3-(2-Propylidene)-1,4-pentadiene	129 ^l		129.5	−0.5			87.5		8220.3		8219.9	0.5
C ₉ H ₁₂	4,4-Dimethyl-1,2,5,6-heptatetraene	340 ^l		340.9	−0.9			296.1		8726.0		8725.1	0.9
<i>Diyne, alkenynes</i>													
C ₄ H ₂	1,3-Butadiyne	464 ^o		461.2	2.8			426.8		2838.7		2841.5	−2.8
C ₅ H ₆	(Z)-3-Penten-1-yne	258 ^l		260.6	−2.6	226.5	4.6	229.0	−2.5	4633.3		4630.8	2.6
	(E)-3-Penten-1-yne	259 ^l		256.4	2.6	228.2	1.8	225.7	2.5	4632.3		4634.9	−2.6
C ₆ H ₆	2,4-Hexadiyne	377.4 ^p		380.2	−2.8	335.2 ^p	5.0	334.6	0.6	5230.6		5227.8	2.8
C ₇ H ₈	3,3-Dimethyl-1,4-pentadiyne			384.1		348.7	3.4	347.3	1.4			6376.6	

(continued on next page)

TABLE 6 (continued)

Compound		Experimental gas-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase standard molar enthalpy of formation		Experimental liquid-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted liquid-phase standard molar enthalpy of formation		Experimental standard molar enthalpy of atomization ^b		Estimated value and difference between exp. and fitted standard molar enthalpy of atomization	
Formula	Name	Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₈ H ₁₂	1-Octen-3-yne			185.7		140.7	6.4	140.2	0.5			8163.8	
C ₁₀ H ₁₀	Diisopropenyldiacetylene	494.1 ^q		494.1	0.0	444 ^q	2	444.0	0.0	8852.6		8852.6	0.0
C ₁₀ H ₁₆	(Z)-3-Decen-1-yne			156.9		99.2	2.4	101.8	−2.6			10497.7	
	(E)-3-Decen-1-yne			152.8		100.5	1.5	98.4	2.1			10501.9	
C ₁₂ H ₁₈	3,3,6,6-Tetramethyl-1,7-octadiyne			268.8		211.1	5.2	211.7	−0.6			12255.1	
	5,7-Dodecadiyne			255.2		181.5	3.6	181.2	0.3			12268.8	
	2,2,7,7-Tetramethylocta-3,5-diyne			220.8		156.1	1.8	157.0				12303.4	
<i>Cycloalkanes</i>													
C ₃ H ₆	Cyclopropane	53.3	0.5	54.3	−1.0	35.2	2.5	37.3	−2.1	3404.7	0.5	3403.8	0.9
C ₄ H ₈	Methylcyclopropane			−9.6		1.7	0.6	1.9	−0.2			4620.2	
	Cyclobutane	27.7	1.1	27.7	0.0	3.7	0.5	3.7	0.0	4583.0	1.1	4583.0	0.0
C ₅ H ₈	Ethenylcyclopropane	127 ^l		125.1	1.9	102.5 ^r	0.8	100.8	1.7	5200.3		5202.3	−1.9
C ₅ H ₁₀	Ethylcyclopropane			0.9		−24.8	0.7	−24.8	0.0			5762.5	
	1,1-Dimethylcyclopropane	−8.2	1.1	−8.2	0.0	−33.3	0.7	−36.0	2.7	5771.5	1.1	5771.5	0.0
	cis-1,2-Dimethylcyclopropane			−65.5		−26.3	0.6	−27.8	1.5			5828.7	
	trans-1,2-Dimethylcyclopropane			−69.1		−30.7	0.7	−29.3	−1.4			5832.3	
	Cyclopentane	−76.4	0.7	−76.5	0.1	−105.1	0.7	−103.4	−1.7	5839.7	0.7	5839.6	0.1
C ₆ H ₁₂	Ethylcyclobutane	−27.5	0.9	−27.5	0.0	−59.0	0.7	−59.0	0.0	6943.5	0.9	6943.5	0.0
	Methylcyclopentane	−106.2	0.7	−108.9	2.7	−137.9	0.7	−139.5	1.6	7022.2	0.7	7024.9	−2.7
	Cyclohexane	−123.3	0.8	−123.5	0.2	−156.4	0.8	−156.2	−0.2	7039.3	0.8	7039.4	−0.1
C ₇ H ₁₂	Ethenylcyclopentane			−3.0		−34.8	1.0	−37.3	2.5			7635.6	
C ₇ H ₁₄	cis-1,2-Diethylcyclopropane	−44.6 ^s	1.6	−44.6	0.0	−79.9	1.3	−81.1	1.2	8113.3	1.6	8113.3	0.0
	trans-1,2-Diethylcyclopropane	−49.1 ^s	1.8	−48.1	−1.0	−83.3	2.1	−82.6	−0.7	8117.8	1.8	8116.8	0.9
	1,1-Dimethyl-2-ethylcyclopropane			−48.9		−90.2	0.9	−89.5	−0.7			8117.6	
	Ethylcyclopentane	−126.9	1.0	−127.2	0.3	−163.4	1.0	−162.9	−0.5	8195.6	1.0	8195.8	−0.3
	1,1-Dimethylcyclopentane	−138.2	1.0	−137.3	−0.9	−172.1	1.0	−172.9	0.8	8206.9	1.0	8206.0	0.8
	cis-1,2-Dimethylcyclopentane	−129.5	1.3	−129.3	−0.2	−165.3	1.3	−166.4	1.1	8198.2	1.3	8197.9	0.3
	trans-1,2-Dimethylcyclopentane	−136.6	1.1	−137.0	0.4	−171.2	1.1	−171.4	0.2	8205.3	1.1	8205.8	−0.5
	trans-1,3-Dimethylcyclopentane	−133.6	1.4	−133.6	0.0	−168.1	1.4	−168.1	0.0	8202.3	1.4	8202.3	−0.1
	Methylcyclohexane	−154.6	1.0	−154.0	−0.6	−190.1	1.0	−189.5	−0.6	8223.3	1.0	8222.6	0.7
	Cycloheptane	−118.1	0.9	−118.1	0.0	−156.6	0.9	−156.6	0.0	8186.8	0.9	8186.8	0.0
C ₈ H ₁₄	2-Propenylcyclopentane	−24.1	2.6	−22.7	−1.4	−64.5	2.6	−62.5	−2.0	8809.4	2.6	8808.0	1.5
	Ethenylcyclohexane	−48.9	0.8	−48.1	−0.8	−88.7	0.8	−87.3	−1.4	8834.2	0.8	8833.4	0.9
C ₈ H ₁₆	1,1-Dimethyl-2-propylcyclopropane			−69.7		−116.0	1.7	−115.1	−0.9			9291.0	
	Propylcyclopentane	−147.7	1.0	−148.0	0.3	−188.8	1.0	−188.5	−0.3	9369.0	1.0	9369.3	−0.2
	1-Ethyl-1-methylcyclopentane			−151.9		−193.8	1.0	−193.0	−0.8			9373.3	
	cis-1-Ethyl-2-methylcyclopentane			−147.6		−190.8	1.0	−189.7	−1.1			9368.8	
	trans-1-Ethyl-2-methylcyclopentane	−156.2	0.9	−155.3	−0.9	−195.1	0.9	−194.8	−0.3	9377.5	0.9	9376.7	0.8
	1,1-Dimethylcyclohexane	−180.8	2.0	−180.8	0.0	−218.7	1.9	−219.4	0.7	9402.1	2.0	9402.2	0.0
	cis-1,2-Dimethylcyclohexane	−172.1	1.8	−172.0	−0.1	−211.8	1.8	−211.8	0.0	9393.4	1.8	9393.4	0.1
	trans-1,2-Dimethylcyclohexane	−179.8	1.8	−180.1	0.3	−218.2	1.8	−218.7	0.5	9401.1	1.8	9401.5	−0.3
	cis-1,3-Dimethylcyclohexane	−184.6	1.7	−184.5	−0.1	−222.9	1.7	−222.8	−0.1	9405.9	1.7	9405.8	0.1
	trans-1,3-Dimethylcyclohexane	−176.5	1.7	−176.4	−0.1	−215.7	1.7	−216.0	0.3	9397.8	1.7	9397.7	0.1
	cis-1,4-Dimethylcyclohexane	−176.5	1.7	−176.4	−0.1	−215.6	1.7	−216.0	0.4	9397.8	1.7	9397.7	0.1

C ₉ H ₁₈	<i>trans</i> -1,4-Dimethylcyclohexane	−184.4	1.7	−184.5	0.1	−222.4	1.7	−222.8	0.4	9405.7	1.7	9405.8	−0.1
	Ethylcyclohexane	−171.5	1.5	−172.3	0.8	−212.1	1.5	−212.8	0.7	9392.8	1.5	9393.6	−0.7
	Cyclooctane	−124.4	1.0	−124.4	0.0	−167.7	1.0	−167.7	0.0	9345.7	1.0	9345.7	0.0
	(1 α ,3 α ,5 α)-1,3,5-Trimethylcyclohexane	−215.4 ^t		−215.0	−0.4			−256.1		10589.4		10589.1	0.4
	(1 α ,3 α ,5 β)-1,3,5-Trimethylcyclohexane	−206.6 ^t		−206.9	0.3			−249.3		10580.6		10580.9	−0.3
	Propylcyclohexane	−192.3	1.0	−193.0	0.7	−237.4	1.0	−238.5	1.1	10566.3	1.0	10567.0	−0.7
	1-Ethyl-1-methylcyclohexane			−195.4		−240.2	1.0	−239.5	−0.7			10569.5	
	<i>cis</i> -1-Ethyl-2-methylcyclohexane			−190.3		−236.2	1.0	−235.1	−1.1			10564.3	
	<i>trans</i> -1-Ethyl-2-methylcyclohexane			−198.4		−240.3	0.9	−242.0	1.7			10572.4	
	<i>cis</i> -1-Ethyl-3-methylcyclohexane			−202.8		−247.1	1.1	−246.2	−0.9			10576.8	
	<i>cis</i> -1-Ethyl-4-methylcyclohexane			−194.7		−238.9	1.0	−239.3	0.4			10568.7	
	<i>trans</i> -1-Ethyl-4-methylcyclohexane			−202.8		−246.4	0.9	−246.2	−0.2			10576.8	
	Cyclononane	−132.8	1.5	−132.8	0.0	−181.2	1.0	−181.2	0.0	10506.8	1.5	10506.8	0.0
C ₁₀ H ₂₀	Butylcyclohexane	−213.7	1.3	−213.8	0.1	−263.1	1.3	−264.1	1.0	11740.4	1.3	11740.4	0.0
	Cyclodecane	−154.3	1.5	−154.3	0.0	−206.7	0.9	−206.7	0.0	11681.0	1.5	11681.0	0.0
C ₁₁ H ₂₂	1,1-Dimethyl-2-hexylcyclopropane			−131.9		−193.0	1.7	−191.9	−1.1			12811.3	
	Cycloundecane	−179.4	1.7	−179.4	0.0	−235.5	1.1	−235.5	0.0	12858.7	1.7	12858.8	0.0
C ₁₂ H ₂₄	Cyclododecane	−230.3	2.1	−230.3	0.0			−307.1		14062.3	2.1	14062.3	0.0
C ₁₃ H ₂₆	Cyclotridecane	−246.4	2.0	−246.4	0.0	−309.7	1.5	−309.7	0.0	15231.1	2.0	15231.1	0.0
C ₁₄ H ₂₈	<i>trans</i> -1,4-Di- <i>tert</i> -butylcyclohexane			−321.1		−384.9	1.3	−384.3	−0.6			16458.3	
	1,1,4,4-Tetramethylcyclodecane			−271.0		−338.0	1.3	−338.0	0.0			16408.1	
	1,1,5,5-Tetramethylcyclodecane			−271.0		−328.6	1.8	−328.6	0.0			16408.1	
	Cyclotetradecane	−275.7 ^u	2.3	−275.7	0.0			−358.4		16413.1	2.3	16413.1	0.0
C ₁₅ H ₃₀	Decylcyclopentane			−293.3		−367.3	2.3	−367.7	0.4			17583.2	
	Cyclopentadecane	−301.4	1.7	−301.4	0.0			−384.0		17591.4	1.7	17591.4	0.0
C ₁₆ H ₃₂	Cyclohexadecane	−321.7	2.0	−321.7	0.0			−409.7		18764.4	2.0	18764.4	0.0
C ₁₇ H ₃₄	Cycloheptadecane	−364.3	2.1	−364.3	0.0			−435.3		19959.7	2.1	19959.7	0.0
Alkylidenecycloalkanes													
C ₄ H ₆	Methylenecyclopropane	200.5	1.8	200.5	0.0			85.9		3974.2	1.8	3974.2	0.0
C ₅ H ₈	Methylenecyclobutane	121.6	0.7	121.6	0.0	93.8	0.5	93.8	0.0	5205.7	0.7	5205.7	0.0
C ₆ H ₁₀	Methylenecyclopentane	12.0	1.0	12.7	−0.7	−20.1	0.8	−20.0	−0.1	6468.0	1.0	6467.5	0.5
C ₇ H ₁₂	Ethylidenecyclopentane	−18.1	0.9	−18.6	0.5	−56.7	0.8	−57.0	0.3	7650.8	0.9	7651.3	−0.5
C ₈ H ₁₄	Ethylidenecyclohexane	−59.5	0.8	−59.5	0.0	−103.5	0.7	−103.5	0.0	8844.8	0.8	8845.3	−0.5
Cycloalkenes													
C ₃ H ₄	Cyclopropene	277.1	2.5	277.1	0.0					2744.9	2.5	2744.9	0.0
C ₄ H ₆	1-Methylcyclopropene	243.6	1.1	243.6	0.0			39.2		3931.1	1.1	3931.0	0.0
	Cyclobutene	156.7	1.5	156.7	0.0			65.7		4018.0	1.5	4017.9	0.1
C ₅ H ₆	1,3-Cyclopentadiene	134.3	1.5	134.4	−0.1	105.9	1.5	105.7	0.2	4757.0	1.5	4757.0	0.0
C ₅ H ₈	Cyclopentene	34.0	1.4	33.9	0.1	4.3	0.8	4.5	−0.2	5293.3	1.4	5293.5	−0.1
C ₆ H ₈	3-Methylenecyclopentene	115 ^l		115.0	0.0			81.8		5929.0		5929.2	−0.2
	1,3-Cyclohexadiene	104.6 ^v	0.6	104.9	−0.3	71.4 ^v	0.6	71.3	0.1	5939.4	0.6	5939.1	0.4
	1,4-Cyclohexadiene	104.8 ^v	0.6	104.9	−0.2	69.7 ^v	0.6	69.3	0.4	5939.3	0.6	5939.1	0.1
C ₆ H ₁₀	1-Methylcyclopentene	−3.8	0.8	−3.6	−0.2	−36.4	0.6	−36.0	−0.4	6483.8	0.8	6483.7	0.2
	3-Methylcyclopentene	7.4	0.6	6.8	0.6	−23.7	0.6	−22.9	−0.8	6472.6	0.6	6473.1	−0.5
	Cyclohexene	−4.3 ^w	1.0	−5.2	0.9	−37.8 ^w	0.8	−39.0	1.2	6484.3	1.0	6485.1	−0.8
C ₇ H ₈	1,3,5-Cycloheptatriene	180.9	2.1	180.9	0.0	142.2	2.1	142.2	0.0	6579.8	2.1	6579.8	0.0
C ₇ H ₁₀	3-(<i>cis</i> -Ethylidene)-1-cyclopentene	84.5 ^l		83.6	0.9			44.8		7112.2		7113.0	−0.9
	5,5-Dimethyl-1,3-cyclopentadiene	86.6 ^l		85.7	0.9			49.9		7110.1		7111.0	−0.9
	1,3-Cycloheptadiene	94.3	1.1	94.3	0.0			58.7		7102.4	1.1	7102.4	0.0
C ₇ H ₁₂	1,2-Dimethylcyclopentene	−41.4 ^x	0.8	−42.0	0.6			−82.0		7674.1	0.8	7674.8	−0.7

(continued on next page)

TABLE 6 (continued)

Compound		Experimental gas-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase standard molar enthalpy of formation		Experimental liquid-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted liquid-phase standard molar enthalpy of formation		Experimental standard molar enthalpy of atomization ^b		Estimated value and difference between exp. and fitted standard molar enthalpy of atomization	
Formula	Name	Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₈ H ₈	1-Ethylcyclopentene	−25.0 ^x		−23.8	−1.2	−58.3	0.8	−60.3	2.0	7657.7		7656.3	1.4
	3-Ethylcyclopentene	−12.4 ^x	0.5	−11.5	−0.9			−46.3		7645.1	0.5	7644.1	1.0
	1-Methylcyclohexene	−43.3	0.7	−42.9	−0.4	−81.2	0.7	−81.3	0.1	7676.0	0.7	7675.6	0.4
	4-Methylcyclohexene			−35.7		−75 ^y	4	−72.3	−2.7			7668.4	
	Cycloheptene	−9.2	1.1	−9.2	0.0	−41 ^z		−41.0	0.0	7641.9	1.1	7641.9	0.0
C ₈ H ₈	1,3,5,7-Cyclooctatetraene	295.9	1.7	295.9	0.0	254.5	1.3	254.5	0.0	7181.5	1.7	7181.5	0.0
C ₈ H ₁₀	1,2-Diethenylcyclobutene	262 ⁿ		262.0	0.0			167.7		7651.4		7651.4	0.0
	5-(1-Methylethylidene)-1,3-cyclopentadiene	134.4	5.4	135.2	−0.8	90.0	5.0	90.1	−0.1	7779.0	5.4	7778.1	0.9
	1,3,6-Cyclooctatriene	196.3 ^{aa}		196.3	0.0			97.3		7717.1		7717.0	0.0
C ₈ H ₁₂	3-(2-Propylidene)-1-cyclopentene	49.4 ^l		49.3	0.1			4.1		8299.9		8299.9	0.1
	4-Ethenylcyclohexene	69.5 ^{bb}	1.5	70.2	−0.7	29.7 ^{bb}	1.3	29.9	−0.2	8279.8	1.5	8279.1	0.8
	(Z,Z)-1,3-Cyclooctadiene	84.1 ^l		84.4	−0.3			41.9		8265.2		8264.9	0.3
	(Z,E)-1,3-Cyclooctadiene	146 ^l		143.8	2.2			3.8		8203.3		8205.5	−2.2
	(Z,Z)-1,5-Cyclooctadiene	101.1	1.3	100.8	0.3	57.7	1.3	57.7	0.0	8248.2	1.3	8248.5	−0.3
	(E,E)-1,5-Cyclooctadiene	196 ^l		196.0	0.0			19.5		8153.3		8153.3	0.0
	(E,Z)-1,5-Cyclooctadiene	158 ^l		160.2	−2.2			19.5		8191.3		8189.1	2.2
	1,2,3-Trimethylcyclopentene			−71.3		−118 ^z		−117.2	−0.8			8857.2	
C ₈ H ₁₄	1-Ethylcyclohexene	−63.4	1.0	−63.1	−0.3	−106.7	1.0	−105.7	−1.0	8848.7	1.0	8848.2	0.5
	cis-Cyclooctene	−27.0	1.2	−27.0	0.0	−74.0	1.9	−74.1	0.1	8812.3	1.2	8812.3	0.0
	trans-Cyclooctene	19.6 ^{cc}	3.0	19.6	0.0			−74.1		8765.7	3.0	8765.8	0.0
C ₉ H ₁₂	(Z,Z,Z)-1,4,7-Cyclononatriene	189 ^l		189.0	0.0			131.1		8877.0		8877.0	0.0
C ₉ H ₁₆	(E)-1-Methyl-1-cyclooctene	−5.4 ^l		−5.4	0.0			−101.7		9943.4		9943.4	0.0
C ₁₀ H ₁₂	1,2,6,7-Cyclodecatetraene	356.1 ^{dd}	3.8	356.1	0.0			585.1		9426.6	3.8	9426.6	0.0
	meso-1,2,6,7-Cyclodecatetraene	360 ^l		360.0	0.0			585.1		9422.7		9422.7	0.0
C ₁₀ H ₁₄	1,2,3,4-Tetramethyl-5-methylene-1,3-cyclopentadiene	83.3 ^l		83.2	0.1			11.5		10135.4		10135.5	−0.1
C ₁₀ H ₁₆	1-Methyl-4-(1-methylethenyl)cyclohexene	−2.6	2.9	−2.6	0.0	−50.8	2.1	−50.8	0.0	10657.3	2.9	10657.5	−0.2
	5-Isopropyl-2-methyl-1,3-cyclohexadiene	−9.3	3.4	−10.1	0.8	−60.0	4.0	−60.7	0.7	10664.0	3.4	10664.9	−0.9
	1-Isopropyl-4-methyl-1,3-cyclohexadiene	−20.6	3.4	−20.6	0.0			−66.8		10675.3	3.4	10675.3	0.0
C ₁₀ H ₁₈	1-Methyl-4-(1-methylethyl)cyclohexene	−110.8 ^{ee}	3.2	−110.7	−0.1	−159.8 ^{ee}	3.2	−160.0	0.2	11201.5	3.2	11201.4	0.1
C ₁₂ H ₁₈	(E,E,Z)-1,5,9-Cyclododecatriene	97.1	4.3	97.1	0.0	29.9	4.2	29.9	0.0	12426.9	4.3	12426.9	0.0
	(E,E,E)-1,5,9-Cyclododecatriene	101.3	4.3	101.3	0.0			29.9		12422.7	4.3	12422.7	0.0
Benzene derivatives													
C ₆ H ₆	Benzene	82.6	0.7	83.3	−0.7	49.0	0.5	49.0	0.0	5525.4	0.7	5524.6	0.8
C ₇ H ₈	Methylbenzene	50.5	0.5	50.3	0.2	12.4	0.5	11.3	1.1	6710.2	0.5	6710.4	−0.2
C ₈ H ₆	Phenylacetylene	306.6 ^{ff}	1.7	306.6	0.0	283.5	4.2	283.5	0.0	6734.8	1.7	6734.8	0.0
C ₈ H ₈	Phenylethylene	148.0	1.4	148.0	0.0	103.8	1.1	103.8	0.0	7329.4	1.4	7329.4	−0.1
C ₈ H ₁₀	Ethylbenzene	30.0	1.0	30.4	−0.4	−12.3	0.8	−12.0	−0.3	7883.4	1.0	7883.0	0.4
	1,2-Dimethylbenzene	19.1	1.0	18.9	0.2	−24.4	1.0	−23.3	−1.1	7894.3	1.0	7894.5	−0.2
	1,3-Dimethylbenzene	17.3	0.7	17.2	0.1	−25.4	0.7	−26.4	1.0	7896.1	0.7	7896.1	0.0
	1,4-Dimethylbenzene	18.1	1.0	17.2	0.9	−24.4	1.0	−26.4	2.0	7895.3	1.0	7896.1	−0.8
C ₉ H ₁₀	2-Phenylpropene	118.3 ^{gg}	1.4	118.3	0.0	70.5	1.1	70.5	0.0	8511.7	1.4	8511.7	0.0

C ₉ H ₁₂	Propylbenzene	7.9	0.7	9.6	−1.7	−38.3	0.7	−37.6	−0.7	9058.1	0.7	9056.4	1.7
	(1-Methylethyl)benzene	4.0	1.0	2.0	2.0	−41.1	1.0	−40.8	−0.3	9062.0	1.0	9064.1	−2.1
	1-Ethyl-2-methylbenzene	1.3	1.0	−1.1	2.4	−46.4	1.0	−46.7	0.3	9064.7	1.0	9067.1	−2.4
	1-Ethyl-3-methylbenzene	−1.8	1.1	−2.7	0.9	−48.7	1.1	−49.7	1.0	9067.8	1.1	9068.7	−0.9
	1-Ethyl-4-methylbenzene	−3.2	1.3	−2.7	−0.5	−49.8	1.3	−49.7	−0.1	9069.2	1.3	9068.7	0.5
	1,2,3-Trimethylbenzene	−9.5	1.2	−11.5	2.0	−58.5	1.2	−57.8	−0.7	9075.5	1.2	9077.5	−1.9
	1,2,4-Trimethylbenzene	−13.9	1.0	−14.2	0.3	−61.8	1.0	−61.0	−0.8	9079.9	1.0	9080.2	−0.3
	1,3,5-Trimethylbenzene	−15.9	1.3	−15.8	−0.1	−63.4	1.3	−64.1	0.7	9081.9	1.3	9081.8	0.1
C ₁₀ H ₁₄	Butylbenzene	−11.8	1.2	−11.1	−0.7	−63.2	1.0	−63.2	0.0	10230.5	1.2	10229.8	0.7
	(1-Methylpropyl)benzene	−18.4	1.5	−16.4	−2.0	−66.4	1.2	−64.1	−2.3	10237.1	1.5	10235.0	2.1
	<i>tert</i> -Butylbenzene	−23.0	1.5	−23.0	0.0	−70.7	1.2	−70.7	0.0	10241.7	1.5	10241.7	0.0
	1-Methyl-2-propylbenzene			−21.8		−72.5	0.9	−72.3	−0.2			10240.5	
	1-Methyl-3-propylbenzene			−23.4		−76.2	1.1	−75.3	−0.9			10242.1	
	1-Methyl-4-propylbenzene			−23.4		−75.1	0.9	−75.3	0.2			10242.1	
	1,2-Diethylbenzene			−21.0		−68.5	0.9	−70.0	1.5			10239.7	
	1,3-Diethylbenzene			−22.6		−73.5	1.0	−73.0	−0.5			10241.3	
	1,4-Diethylbenzene			−22.6		−72.8	0.9	−73.0	0.2			10241.3	
	1-Isopropyl-2-methylbenzene			−29.5		−73.3	0.9	−75.5	2.2			10248.2	
	1-Isopropyl-3-methylbenzene			−31.1		−78.6	1.0	−78.5	−0.1			10249.8	
	1-Isopropyl-4-methylbenzene			−31.1		−78.0	1.0	−78.5	0.5			10249.8	
	1-Ethyl-2,3-dimethylbenzene			−31.4		−80.5	1.2	−81.1	0.6			10250.1	
	2-Ethyl-1,3-dimethylbenzene			−31.4		−80.1	1.2	−81.1	1.0			10250.1	
	4-Ethyl-1,2-dimethylbenzene			−34.1		−86.0	1.0	−84.4	−1.6			10252.8	
	1-Ethyl-2,4-dimethylbenzene			−34.1		−84.1	1.2	−84.4	0.3			10252.8	
	2-Ethyl-1,4-dimethylbenzene			−34.1		−84.8	1.1	−84.4	−0.4			10252.8	
	1-Ethyl-3,5-dimethylbenzene			−35.7		−87.8	1.1	−87.4	−0.4			10254.4	
	1,2,3,4-Tetramethylbenzene			−38.3		−90.2	1.2	−90.2	0.0			10257.0	
	1,2,3,5-Tetramethylbenzene			−44.5		−96.4	1.1	−95.5	−0.9			10263.2	
	1,2,4,5-Tetramethylbenzene	−47.1	1.9	−45.6	−1.5			−95.7		10265.8	1.9	10264.3	1.5
C ₁₁ H ₁₆	Pentylbenzene			−31.9		−89.4	4.2	−88.8	−0.6			11403.2	
	Pentamethylbenzene	−67.2	2.2	−65.2	−2.0			−122.6		11438.6	2.2	11436.6	1.9
	1- <i>tert</i> -Butyl-2-methylbenzene	−33 ^{hh}	2	−33.0	0.0			−114.6		11404.4	2	11404.3	0.0
C ₁₂ H ₁₈	Hexamethylbenzene	−77.4	2.5	−78.1	0.7			−145.4		12601.4	2.5	12602.1	−0.7
<i>Biphenyl compounds</i>													
C ₁₂ H ₁₀	Biphenyl	178.2 ^{ii,jj}	2.6	180.0	−1.8			118.5		10601.8	2.6	10600.0	1.8
C ₁₃ H ₁₂	2-Methylbiphenyl	152.8 ^{kk}	1.5	152.8	0.0	86.5 ^{kk}	1.3	86.5	0.0	11779.9	1.5	11779.9	0.0
C ₁₄ H ₁₄	4,4'-Dimethylbiphenyl	111.3 ^{ll}	3.6	113.9	−2.6			43.1		12974.1	3.6	12971.5	2.6
C ₁₆ H ₁₈	4- <i>tert</i> -Butylbiphenyl	72.0 ^{mm}	2.8	73.6	−1.6			−1.3		15318.7	2.8	15317.1	1.6
C ₁₈ H ₁₄	3-Phenylbiphenyl	279.9 ⁿⁿ	2.0	276.6	3.3	192.8 ⁿⁿ	1.2	187.9	4.9	15672.1	2.0	15675.4	−3.3
	4-Phenylbiphenyl	279.0 ^{oo}	6.3	276.6	2.4	187.7 ⁿⁿ	0.9	187.9	−0.2	15673.0	6.3	15675.4	−2.4
C ₂₀ H ₂₆	4,4'-di- <i>tert</i> -Butylbiphenyl	−35.3 ^{mm}	4.0	−32.7	−2.6	−122.1 ^{mm}	2.4	−121.0	−1.1	20036.7	4.0	20034.2	2.5
C ₂₄ H ₁₈	1,3,5-Triphenylbenzene	372.3 ⁿⁿ	1.5	373.2	−0.9	254.6 ⁿⁿ	1.2	257.4	−2.8	20751.8	1.5	20750.8	1.0
<i>Polyphenyl compounds</i>													
C ₁₃ H ₁₂	Diphenylmethane	164.8 ^{kk}	1.6	165.5	−0.7	97.1 ^{kk}	1.4	98.0	−0.9	11767.9	1.6	11767.0	0.9
C ₁₄ H ₁₄	4-Methyldiphenylmethane	131.0 ^{pp}	1.2	132.5	−1.5	61.5	1.1	60.3	1.2	12954.4	1.2	12952.7	1.6
C ₁₅ H ₁₆	2,5-Dimethyldiphenylmethane			101.1		24.7	1.3	25.6	−0.9			14136.8	
	2-Ethyldiphenylmethane			110.3		30 ^{qq}		30.7	−0.7			14109.0	
C ₁₉ H ₁₆	Triphenylmethane	267.9 ^{rr,ss}	4.1	266.4	1.5			189.2		16836.8	4.1	16838.2	−1.4

(continued on next page)

TABLE 6 (continued)

Compound		Experimental gas-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted gas-phase standard molar enthalpy of formation		Experimental liquid-phase standard molar enthalpy of formation ^a		Estimated value and difference between exp. and fitted liquid-phase standard molar enthalpy of formation		Experimental standard molar enthalpy of atomization ^b		Estimated value and difference between exp. and fitted standard molar enthalpy of atomization	
Formula	Name	Value	Error	Value	Diff.	Value	Error	Value	Diff.	Value	Error	Value	Diff.
C ₂₀ H ₁₈	1,1,1-Triphenylethane	265.8 ^{tt}	2.3	262.2	3.6	177.2 ^{tt}	2.1	173.8	3.3	17991.6	2.3	17995.2	−3.6
	1,1,2-Triphenylethane	246.8 ^{tt}	2.2	246.6	0.2			161.8		18010.6	2.2	18010.6	0.0
C ₂₅ H ₂₀	Tetraphenylmethane	397.8	4.9	400.4	−2.6	295.4 ^{tt}	2.5	297.1	−1.7	21878.9	4.9	21876.4	2.5

^a Values taken from Pedley [13], unless stated otherwise.

^b The enthalpy of atomization was calculated as the enthalpy change associated with equation (1) (see text) using the gas-phase standard molar enthalpy of formation of the compound $\Delta_f H_m^\circ(\text{H}, \text{g}) = 217.999 \pm 0.006 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_f H_m^\circ(\text{C}, \text{g}) = 716.67 \pm 0.46 \text{ kJ} \cdot \text{mol}^{-1}$ [22].

^c Reference [23].

^d Reference [24].

^e Calculated using data from NIST Chemistry WebBook [20].

^f Reference [25].

^g Reference [26].

^h Reference [27].

ⁱ Reference [28].

^j Reference [29].

^k Reference [30].

^l Reference [31].

^m Reference [32].

ⁿ Reference [33].

^o Reference [34].

^p Reference [35].

^q Reference [36].

^r Reference [37].

^s Reference [38].

^t Reference [39].

^u Reference [40].

^v Reference [41].

^w Reference [42].

^x Reference [43].

^y Reference [44].

^z Reference [45].

^{aa} Reference [46].

^{bb} Reference [47].

^{cc} Reference [48].

^{dd} Reference [49].

^{ee} Reference [50].

^{ff} Reference [51].

^{gg} Reference [52].

^{hh} Reference [53].

ⁱⁱ Reference [54].

^{jj} Reference [55].

^{kk} Reference [56].

^{ll} Reference [57].

^{mm} Reference [58].

ⁿⁿ Reference [59].

^{oo} Reference [60].

^{pp} Reference [61].

^{qq} Reference [62].

^{rr} Reference [63].

^{ss} Reference [64].

^{tt} Reference [65].

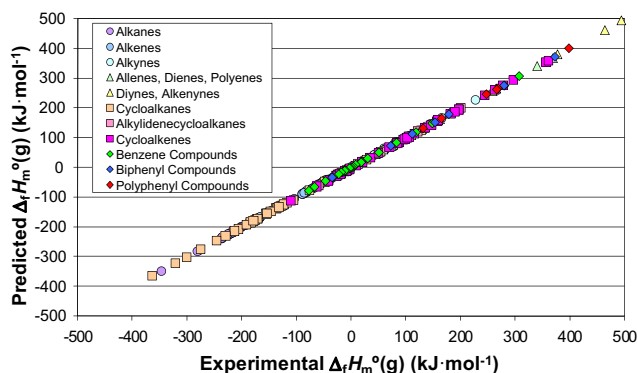


FIGURE 14. Estimated versus experimental standard molar enthalpies of formation for gas-phase compounds. The correlation coefficient of the linear fit is 0.99998.

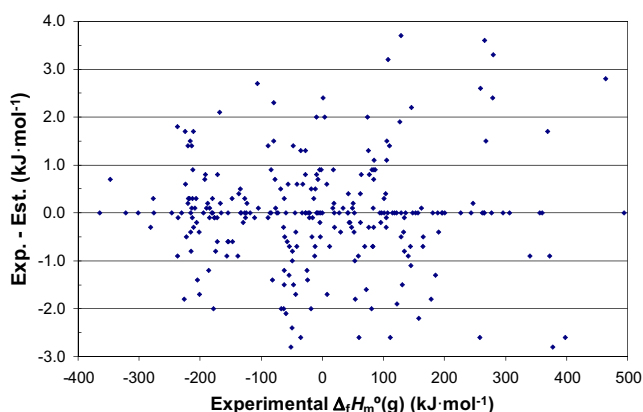


FIGURE 15. Differences between experimental and estimated standard molar enthalpies of formation for gas-phase compounds as a function of the experimental enthalpy of formation.

265 standard molar enthalpies of atomization, all at $T = 298.15$ K) led to three sets of 165 ELBA parameters (table 7), two of them for gas- and liquid-phase standard molar enthalpies of formation, and the other for the standard molar enthalpies of atomization.

Due to the lack of experimental data, some of the parameters could not be evaluated (marked as n.a.). Columns five and six of table 7 display how many times each parameter was used to describe the energetics of the compounds listed in table 6. A low number means that the parameter was seldom used and therefore is more prone to change when data for new compounds become available; a large number means that a parameter was widely used and so its value should be robust. To predict the desired property for a given compound, a sum of all the suitable parameters in the molecule must be made. The parameters in table 7 are given with two decimals, to avoid round-off errors. To minimize these errors when predicting a value, a Microsoft® Office Excel datasheet is supplied as Supplementary material.

Figure 14 summarizes the types of compounds covered by the ELBA method and shows that the estimated standard enthalpies of formation span a wide range. Figure 15 shows the differences between the experimental and estimated gas-phase standard molar enthalpies of formation. The average absolute difference between the estimated and the experimental values is $0.73 \text{ kJ} \cdot \text{mol}^{-1}$ for the 265 gas-phase compounds, and $0.79 \text{ kJ} \cdot \text{mol}^{-1}$ for the 242 compounds in the liquid phase. The maximum deviations are $3.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $4.9 \text{ kJ} \cdot \text{mol}^{-1}$ for gas- and liquid-phase data,

TABLE 7

Calculated ELBA parameters ($\text{kJ} \cdot \text{mol}^{-1}$) and number of times they were used (frequency).

Parameter	Parameter value			Use frequency	
	$\Delta_f H_m^\circ(\text{g})^a$	$\Delta_f H_m^\circ(\text{l})^a$	$\Delta_{\text{at}} H_m^\circ$	Gas-phase and atomization	Liquid-phase
C3H	17.05	−13.18	393.04	72	88
C2H	−7.18	−13.22	407.26	179	176
C1H	−13.13	−16.70	411.38	197	203
C0H	−18.60	n.a.	415.77	1	0
C1C1	−5.03	6.57	356.68	1	1
C1C2	−5.84	2.36	358.06	88	108
C1C3	−11.20	2.88	362.00	53	64
C1C4	−3.13	2.10	358.22	35	41
C2C2	−6.40	0.84	358.89	118	116
C2C3	−9.31	3.62	360.37	54	68
C2C4	2.43	6.18	352.92	16	24
C3C3	−7.85	10.57	357.48	15	20
C3C4	8.66	16.05	345.31	6	10
C4C4	30.86	29.65	327.44	2	1
Z15	8.43	8.54	−8.35	6	5
D1D1	−1.20	n.a.	523.46	1	0
D1D2	0.83	0.94	518.30	26	19
D1D3	9.71	7.42	513.35	19	15
D2D2	2.86	4.30	513.11	56	37
D2D3	15.19	14.25	504.70	18	14
D3D3	29.05	24.31	494.71	7	3
C1D2	14.59	10.46	388.65	30	21
C1D3	12.92	16.75	390.42	31	24
C2D2	14.20	9.68	389.35	58	39
C2D3	12.99	16.47	390.45	27	19
C3D2	10.23	12.09	391.92	11	11
C3D3	13.14	20.15	389.04	4	4
C4D2	25.94	17.39	380.51	6	4
C4D3	31.95	30.70	374.48	1	1
D1H	13.42	10.75	432.36	51	35
D2H	17.42	20.49	431.94	100	69
Z11	4.11	3.35	−4.13	21	15
Z14	16.11	15.63	−16.07	1	1
Z44	38.52	44.29	−38.42	1	1
T1T1	21.79	25.01	698.53	1	1
T1T2	59.35	62.05	695.48	13	12
T2T2	96.44	95.17	692.96	14	9
C1T2	64.28	62.67	433.60	8	3
C2T2	63.49	61.30	434.69	17	8
C3T2	47.99	63.86	446.13	1	1
C4T2	72.74	67.77	428.43	1	4
T1H	102.46	91.85	472.05	14	13
D1Dd	68.61	−0.56	550.85	6	2
D2Dd	74.14	137.20	542.19	9	1
D3Dd	86.56	146.93	533.50	1	1
DdDd	131.49	n.a.	585.16	2	0
Cd2Cd2	18.40	2.76	436.25	18	6
Cd2Cd3	19.06	10.10	435.54	10	3
Cd3Cd3	25.27	23.25	429.11	2	1
Cd2Ct2	81.74	66.14	467.62	2	5
Cd3Ct2	71.74	71.72	477.50	1	1
Ct2Ct2	137.56	119.06	506.43	3	4
ZS3C2	38.84	38.03	−38.83	8	12
ZS3C3	28.76	27.72	−28.67	3	7
ZS3C3m	n.a.	31.04	n.a.	0	3
ZS3C4	n.a.	n.a.	n.a.	0	0
ZS3C4m	n.a.	n.a.	n.a.	0	0
ZS3C4mm	29.39	23.58	−29.30	1	4
ZS3D3	95.38	n.a.	−95.10	1	0
Z3c12	3.54	1.50	−3.54	1	5
ZS4C2	27.68	26.53	−27.67	5	3
ZS4C3	15.78	15.55	−15.73	1	1
ZS4C4	n.a.	n.a.	n.a.	0	0
ZS4D3	31.88	30.00	−31.57	1	1
Z4c12	n.a.	n.a.	n.a.	0	0
ZS5C2	5.46	4.92	−5.48	22	22
ZS5C3	−1.97	−2.79	2.15	10	13
ZS5C4	−2.37	−5.74	2.66	2	2
ZS5D3	4.97	1.76	−4.32	7	3
Z5c12	7.62	5.07	−7.88	2	2
Z5t13	7.73	7.51	−7.79	1	1
Z1cy	−2.62	−3.18	2.43	5	3

(continued on next page)

Table 7 (continued)

Parameter	Parameter value			Use frequency	
	$\Delta_f H_m^\circ(\text{g})^a$	$\Delta_f H_m^\circ(\text{l})^a$	$\Delta_{\text{at}} H_m^\circ$	Gas-phase and atomization	Liquid-phase
ZS6C2	0.18	−0.43	−0.18	26	31
ZS6C3	−5.34	−5.36	5.43	17	22
ZS6C4	−12.25	−11.67	12.47	1	2
ZS6D3	5.83	2.62	−4.73	1	1
Z6ax	8.11	6.85	−8.11	5	7
ZS7C2	3.89	3.24	−3.87	4	3
ZS7C3	n.a.	n.a.	n.a.	0	0
ZS7C4	n.a.	n.a.	n.a.	0	0
ZS8C2	5.21	4.65	−5.20	10	3
ZS8C3	n.a.	n.a.	n.a.	0	0
ZS8C4	n.a.	n.a.	n.a.	0	0
ZS9C2	6.00	5.47	−5.99	2	1
ZS9C3	n.a.	n.a.	n.a.	0	0
ZS9C4	n.a.	n.a.	n.a.	0	0
ZS10C2	5.33	4.93	−5.32	3	3
ZS10C3	n.a.	n.a.	n.a.	0	0
ZS10C4	n.a.	−1.86	n.a.	0	2
Z10int	n.a.	9.40	n.a.	0	1
ZS11C2	4.45	4.19	−4.44	1	1
ZS11C3	n.a.	n.a.	n.a.	0	0
ZS11C4	n.a.	n.a.	n.a.	0	0
ZS12C2	1.57	0.01	−1.55	3	1
ZS12C3	n.a.	n.a.	n.a.	0	0
ZS12C4	n.a.	n.a.	n.a.	0	0
ZS13C2	1.80	1.78	−1.79	1	1
ZS13C3	n.a.	n.a.	n.a.	0	0
ZS13C4	n.a.	n.a.	n.a.	0	0
ZS14C2	1.07	n.a.	−1.05	1	0
ZS14C3	n.a.	n.a.	n.a.	0	0
ZS14C4	n.a.	n.a.	n.a.	0	0
ZS15C2	0.66	n.a.	−0.65	1	0
ZS15C3	n.a.	n.a.	n.a.	0	0
ZS15C4	n.a.	n.a.	n.a.	0	0
ZS16C2	0.65	n.a.	−0.64	1	0
ZS16C3	n.a.	n.a.	n.a.	0	0
ZS16C4	n.a.	n.a.	n.a.	0	0
ZS17C2	−0.67	n.a.	0.68	1	0
ZS17C3	n.a.	n.a.	n.a.	0	0
ZS17C4	n.a.	n.a.	n.a.	0	0
ZD3D2	93.25	n.a.	−93.26	2	0
ZD3D3	92.53	n.a.	−92.40	1	0
ZD4D2	35.17	n.a.	−35.19	1	0
ZD4D3	27.15	n.a.	−26.87	1	0
ZD5D2	6.86	5.89	−6.90	11	6
ZD5D3	−4.35	−6.52	4.65	4	3
Z5	−6.39	−9.03	6.69	2	2
ZD6D2	0.26	−1.57	−0.23	10	10
ZD6D3	−4.70	−6.80	4.93	6	5
Z6	2.05	2.22	−2.06	9	9
Z6s	−7.09	−3.54	7.23	1	1
ZD7D2	1.33	3.49	−1.32	3	2
ZD7D3	n.a.	n.a.	n.a.	0	0
Z7u13	11.00	n.a.	−11.02	1	0
Z7u135	5.11	−16.30	−5.15	1	1
ZD8D2	−3.10	−6.07	3.11	10	3
ZD8D3	0.57	n.a.	−0.41	1	0
Z8uZZ	30.40	38.18	−30.41	2	1
Z8uE	46.60	n.a.	−46.57	2	0
Z8uZE	89.80	n.a.	−89.81	2	0
Z8uEE	125.60	n.a.	−125.60	1	0
Z8u136	44.90	n.a.	−44.92	1	0
Z8u1357	96.33	110.88	−96.38	1	1
ZD9D2	2.62	n.a.	−2.61	1	0
ZD9D3	n.a.	n.a.	n.a.	0	0
ZD10Cd	3.98	n.a.	−2.99	2	0
ZD10D2	−6.49	n.a.	6.00	2	0
ZD10D3	n.a.	n.a.	n.a.	0	0
Z10u1267	3.90	n.a.	−3.90	1	0
ZD12D2	−0.88	−1.34	0.89	2	1
Z12u159E	4.20	n.a.	−4.20	1	0
A2A2	5.96	3.21	485.01	34	46
A2A3	14.21	13.33	479.63	36	48
A3A3	20.21	17.21	457.97	9	17
C1A3	−2.22	−2.89	398.10	17	27

TABLE 7 (continued)

Parameter	Parameter value			Use frequency	
	$\Delta_f H_m^\circ(\text{g})^a$	$\Delta_f H_m^\circ(\text{l})^a$	$\Delta_{\text{at}} H_m^\circ$	Gas-phase and atomization	Liquid-phase
C2A3	−1.95	−2.12	398.11	9	23
C3A3	−5.83	2.48	400.63	4	5
C4A3	12.64	8.95	386.51	6	4
A2H	7.93	4.96	435.76	37	49
ZA11	3.85	9.26	14.68	4	10
ZA14	25.29	n.a.	−6.81	1	0
ZA44	n.a.	n.a.	n.a.	0	0
ZA1'1	4.42	9.38	14.11	2	5
ZA1'4	n.a.	n.a.	n.a.	0	0
ZA1'1'	8.39	11.54	10.13	2	1
ZA1'4'	n.a.	n.a.	n.a.	0	0
ZA4'1	n.a.	n.a.	n.a.	0	0
ZA4'4'	n.a.	n.a.	n.a.	0	0
D2A3	11.00	−3.45	436.32	1	1
D3A3	16.30	10.60	430.97	1	1
T2A3	52.88	65.28	489.13	1	1
Ca3Ca3	−3.84	−10.17	443.78	8	5
ZA1A	8.11	11.96	10.42	1	1
ZAA	−4.44	0.99	4.46	4	2

^a n.a. – not available.

respectively. When the values for the 11 bi- and polyphenyls compounds are not considered, the maximum deviations become $3.7 \text{ kJ} \cdot \text{mol}^{-1}$ and $2.8 \text{ kJ} \cdot \text{mol}^{-1}$, respectively for gas- and liquid-phase data.

4.2. Values predicted using the obtained parameters

The ELBA method and the obtained parameters can be tested by comparing predicted and experimental standard molar enthalpies of formation of compounds that were not used in our parameterization. A set of such compounds is presented in tables 8 and 9, and their experimental standard molar enthalpies of formation are compared with values predicted by the ELBA method and by two other methods [10,19]. This set includes linear and branched alkanes (nonane, decane, dodecane, hexadecane, and octadecane; 3,3-diethylpentane, 2,2,5-trimethylhexane, 2,3,5-trimethylhexane, and 2-methylnonane), linear and branched alkenes (1-octene, 1-decene, 1-dodecene, and 1-hexadecene; (Z)-2,2-dimethyl-3-hexene, and (E)-2,2-dimethyl-3-hexene), linear alkynes (1-decyne, 2-decyne, and 3-decyne), alkenynes and polyenes ((Z)-hexa-1,5-diyne-3-ene, and (E)-hexa-1,5-diyne-3-ene; (Z)-1,3,5-hexatriene, and (E)-1,3,5-hexatriene), cycloalkanes (bicyclopropyl, bicyclopentyl, dicyclopentylmethane, cyclopentylcyclohexane, bicyclohexyl, decylcyclohexane, and dodecylcyclohexane), and benzene derivatives (cyclopropylbenzene, 4-methyl-1-*tert*-butylbenzene, cyclohexylbenzene, 3,5-dimethyl-1-*tert*-butylbenzene, 1,4-di-*tert*-butylbenzene, 1,1-diphenylcyclopropane, 5-methyl-1,3-di-*tert*-butylbenzene, and decylbenzene).

Very bulky compounds represent a challenge for any additivity method. As an example, our method predicts $-286.8 \text{ kJ} \cdot \text{mol}^{-1}$ for the gas-phase standard molar enthalpy of formation of 3,3,4,4-tetraethylhexane. The only experimental value currently available is $-265.5 \pm 2.6 \text{ kJ} \cdot \text{mol}^{-1}$ [69]. However, it should be stressed that other prediction methods (NIST-S & P and Domalski's) perform even worst (-315 and $-338.9 \text{ kJ} \cdot \text{mol}^{-1}$, respectively).

In every case, the difference between the experimental and estimated values (using the ELBA method) is close to the uncertainties assigned to the experimental values. It should also be stressed the good ability of this method to distinguish between isomers (even between 2- and 3-decyne, for example). Some remarks must, however, be made regarding the global average absolute differences obtained with the methods used for comparison. As stated

TABLE 8

Comparison between experimental and predicted gas-phase standard molar enthalpies of formation at $T = 298.15$ K. Data in $\text{kJ} \cdot \text{mol}^{-1}$.

Compound		Experimental gas-phase enthalpy of formation ^a		Estimated in this paper		Estimated in literature			
Formula	Name	Value	Error	Value	Abs. Diff.	NIST-S & P ^b		Domalski ^c	
						Value	Abs. Diff.	Value	Abs. Diff.
Alkanes									
C ₉ H ₂₀	Nonane	−228.2	0.6	−229.4	1.2	−229	0.8	−228.9	0.7
	3,3-Diethylpentane	−233.3	1.7	−228.6	4.7	−224	9.3	−232.4	0.9
	2,2,5-Trimethylhexane	−253.1	0.9	−253.7	0.6	−250	3.1	−252.7	0.4
	2,3,5-Trimethylhexane	−242.6	0.9	−242.6	0.0	−244	1.4	−246.7	4.1
C ₁₀ H ₂₂	Decane	−249.5	1.3	−250.1	0.6	−250	0.5	−249.6	0.1
	2-Methylnonane	−260.2	2.4	−256.8	3.4	−256	4.2	−256.3	3.9
C ₁₂ H ₂₆	Dodecane	−289.4	2.1	−291.6	2.2	−291	1.6	−290.8	1.4
C ₁₆ H ₃₄	Hexadecane	−374.8	1.9	−374.7	0.1	−374	0.8	−373.3	1.5
C ₁₈ H ₃₈	Octadecane	−414.6	5.6	−416.2	1.6	−415	0.4	−414.6	0.0
	Average difference				1.6		2.5		1.4
Alkenes									
C ₈ H ₁₆	1-Octene	−81.3	1.2	−83.3	2.0	−82.8	1.5	−83.0	1.7
	(Z)-2,2-Dimethyl-3-hexene	−89.3	2.8	−93.2	3.9	−94.6	5.3	−91.6	2.3
	(E)-2,2-Dimethyl-3-hexene	−107.7	1.6	−109.3	1.6	−111	3.3	−108.8	1.1
C ₁₀ H ₂₀	1-Decene	−123.3	1.8	−124.8	1.5	−124	0.7	−124.3	1.0
C ₁₂ H ₂₄	1-Dodecene	−165.4	1.4	−166.4	1.0	−165	0.4	−165.5	0.1
C ₁₆ H ₃₂	1-Hexadecene	−248.4	2.4	−249.4	1.0	−247	1.4	−248.1	0.3
	Average difference				1.8		2.1		1.1
Alkynes									
C ₁₀ H ₁₈	1-Decyne	41.9 ^d	3.4	41.2	0.7	41.8	0.1	42.9	1.0
	2-Decyne	23.6 ^d	3.4	21.4	2.2	23	0.6	n.a. ^e	
	3-Decyne	21.8 ^d	3.3	21.2	0.6	23	1.2	23.8	2.0
	Average difference				1.2		0.6		1.5
Alkenynes, polyenes									
C ₆ H ₄	(Z)-Hexa-1,5-diyne-3-ene	541.8 ^f		528.9	12.9	526.3	15.5	531.3	10.6
	(E)-Hexa-1,5-diyne-3-ene	538.1 ^f		524.8	13.3	526.3	11.8	526.4	11.7
C ₆ H ₈	(Z)-1,3,5-Hexatriene	172 ^g	3	168.8	3.2	166	6	170.6	1.4
	(E)-1,3,5-Hexatriene	168 ^g	3	164.7	3.3	166	2	165.8	2.2
	Average difference				8.2		8.8		6.5
Cycloalkanes									
C ₆ H ₁₀	Bicyclopropyl	129.4	3.5	131.7	2.3	133	3.6	127.0	2.4
C ₁₀ H ₁₈	Bicyclopentyl	−129.0 ^h	0.5	−124.5	4.5	−128	1.0	−128.3	0.7
C ₁₂ H ₂₂	Bicyclohexyl	−215.7	1.5	−214.6	1.1	−222	6.3	−209.4	6.3
C ₁₆ H ₃₂	Decylcyclohexane	−339.5	2.4	−338.4	1.1	−336	3.5	−332.6	6.9
C ₁₈ H ₃₆	Dodecylcyclohexane	−378.6	3.6	−379.9	1.3	−377	1.6	−373.9	4.7
	Average difference				2.1		3.2		4.2
Benzene derivatives									
C ₉ H ₁₀	Cyclopropylbenzene	150.5	1.0	155.8	5.3	162	11.5	152.9	2.4
C ₁₁ H ₁₆	4-Methyl-1- <i>tert</i> -butylbenzene	−57.6 ⁱ	1.0	−56.0	1.6	−57.3	0.3	−61.9	4.3
C ₁₂ H ₁₆	Cyclohexylbenzene	−16.6	1.5	−17.3	0.7	−15	1.6	−15.4	1.2
C ₁₂ H ₁₈	3,5-Dimethyl-1- <i>tert</i> -butylbenzene	−89.9 ⁱ	0.9	−89.1	0.8	−90.8	0.9	−96.2	6.3
C ₁₄ H ₂₂	1,4-di- <i>tert</i> -Butylbenzene	−129.2 ^j	0.6	−129.3	0.1	−131	1.8	−141.8	12.6
C ₁₅ H ₂₄	5-Methyl-1,3-di- <i>tert</i> -butylbenzene	−164.0 ^j	1.0	−162.4	1.6	−164	0.0	−176.2	12.2
C ₁₆ H ₂₆	Decylbenzene	−138.6	2.3	−135.7	2.9	−136	2.6	−136.0	2.7
	Average difference				1.9		2.7		5.9
	Global average difference				2.5		3.1		3.4

^a Values taken from Pedley [13], unless stated otherwise.^b Reference [19].^c Reference [10].^d Reference [26].^e n.a. - not available.^f Reference [31].^g Reference [32].^h Reference [66].ⁱ Reference [67].

above, the compounds presented in tables 8 and 9 were not included in the optimization of ELBA parameters (they are a truly independent test set). Yet, we cannot be sure if this applies to the other two methods. In any case, it is observed that the global average absolute differences obtained by the ELBA method are the smallest both for the gas- and liquid-phase test compounds. For the liquid phase, the NIST-S & P method cannot be applied.

It should also be stressed that the reported standard molar enthalpies of formation for some of the compounds in tables 8 and 9 may be affected by significant experimental errors. This problem will be addressed in a forthcoming paper, where we will assess several experimental standard molar enthalpies of formation for hydrocarbons by using high-level theoretical calculations.

TABLE 9

Comparison between experimental and predicted liquid-phase standard molar enthalpies of formation at $T = 298.15$ K. Data in $\text{kJ} \cdot \text{mol}^{-1}$.

Compound		Experimental liquid-phase enthalpy of formation ^a		Estimated in this paper		Estimated in literature	
Formula	Name	Value	Error	Value	Abs. Diff.	Domalski ^b	Abs. Diff.
<i>Alkanes</i>							
C ₉ H ₂₀	Nonane	−274.7	0.6	−275.5	0.8	−275.3	0.6
	3,3-Diethylpentane	−275.4	1.6	−272.0	3.4	−275.4	0.0
	2,2,5-Trimethylhexane	−293.3	0.9	−293.8	0.5	−293.8	0.5
	2,3,5-Trimethylhexane	−284.0	0.9	−284.2	0.2	−289.0	5.0
C ₁₀ H ₂₂	Decane	−300.9	1.3	−301.1	0.2	−301.1	0.2
	2-Methylnonane	−309.8	2.3	−306.2	3.6	−306.3	3.5
C ₁₂ H ₂₆	Dodecane	−350.9	2.1	−352.3	1.4	−352.5	1.6
C ₁₆ H ₃₄	Hexadecane	−456.1	1.8	−454.8	1.3	−455.4	0.7
	Average difference				1.4		1.5
<i>Alkenes</i>							
C ₈ H ₁₆	1-Octene	−121.8	1.2	−124.0	2.2	−123.5	1.7
	(Z)-2,2-Dimethyl-3-hexene	−126.4	2.8	−130.2	3.8	−129.0	2.6
	(E)-2,2-Dimethyl-3-hexene	−144.9	1.6	−145.8	0.9	−146.5	1.5
C ₁₀ H ₂₀	1-Decene	−173.8	1.8	−175.2	1.4	−174.9	1.1
C ₁₂ H ₂₄	1-Dodecene	−226.2	1.3	−226.4	0.2	−226.4	0.2
C ₁₆ H ₃₂	1-Hexadecene	−328.7	2.4	−328.8	0.1	−329.3	0.6
	Average difference				1.4		1.3
<i>Alkynes, polyenes</i>							
C ₆ H ₈	(E)-1,3,5-Hexatriene	123.1 ^c	10.0	136.7	13.6	132.2	9.1
	Average difference				13.6		9.1
<i>Cycloalkanes</i>							
C ₆ H ₁₀	Bicyclopropyl	95.9	3.3	102.2	6.3	80.7	15.2
C ₁₀ H ₁₈	Bicyclopentyl	−178.9	1.2	−174.1	4.8	−168.2	10.7
C ₁₁ H ₂₀	Dicyclopentylmethane	−205.1	2.1	−203.8	1.3	−193.9	11.2
	Cyclopentylcyclohexane	−230.2	4.2	−224.0	6.2	−219.6	10.6
C ₁₂ H ₂₂	Bicyclohexyl	−273.7	1.4	−274.0	0.3	−271.0	2.7
C ₁₆ H ₃₂	Decylcyclohexane	−418.2	2.3	−417.7	0.5	−414.7	3.5
C ₁₈ H ₃₆	Dodecylcyclohexane	−467.6	3.5	−468.9	1.3	−466.1	1.5
	Average difference				3.0		7.9
<i>Benzene derivatives</i>							
C ₉ H ₁₀	Cyclopropylbenzene	100.3	0.9	112.6	12.3	99.3	1.0
C ₁₁ H ₁₆	4-Methyl-1- <i>tert</i> -butylbenzene	−109.7 ^d	0.9	−108.4	1.3	−114.0	4.3
C ₁₂ H ₁₆	Cyclohexylbenzene	−76.6	1.4	−75.5	1.1	−76.6	0.0
C ₁₂ H ₁₈	3,5-Dimethyl-1- <i>tert</i> -butylbenzene	−146.5 ^d	0.7	−146.1	0.4	−150.6	4.1
C ₁₅ H ₁₄	1,1-Diphenylcyclopropane	185.5	3.3	183.9	1.6	n.a. ^e	
C ₁₆ H ₂₆	Decylbenzene	−218.3	2.3	−216.8	1.5	−218.3	0.0
	Average difference				3.0		1.9
Global average difference					2.6		3.5

^a Values taken from Pedley [13], unless stated otherwise.^b Reference [10].^c Reference [68].^d Reference [67].^e n.a., not available.

5. Conclusion

Based on a model proposed by Laidler [1], a new parameterization (ELBA method) was proposed, allowing the accurate prediction of standard molar enthalpies of formation at $T = 298.15$ K for hydrocarbon compounds in the gas- and liquid-phases, as well as the standard molar enthalpies of atomization. The parameters reported in this paper can be used to estimate those properties for several families of compounds, ranging from linear and highly branched alkanes to cyclic unsaturated hydrocarbons. The accuracy obtained is comparable or better than the obtained with other widely used additivity methods [10,19]. An extension of the ELBA method to other families of compounds, including atoms other than carbon and hydrogen, is now in progress.

The experimental database used to derive the ELBA parameters is largely error free. However, some compounds, not included in that database, show higher than expected deviations and therefore should be subject to further scrutiny. This work is now in progress, by using high-level theoretical calculations.

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Appendix A. Supplementary material

A worksheet to help the calculation of standard molar enthalpies of formation and standard molar enthalpies of atomization at $T = 298.15$ K, based on the ELBA method. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2009.06.013.

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