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# The chemical thermodynamics and diamagnetism of $n$ -alkanes. Calculations up to $n$ -C<sub>110</sub>H<sub>222</sub> from quantum chemical computations and experimental values

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## ABSTRACT

Free energies, enthalpies of formation, enthalpies of combustion, and entropy of  $n$ -alkanes have been determined using quantum-chemical computations. After determination of the scaling factor between experimental results vs ab-initio computations, we are able to give various values corresponding to these thermodynamic properties up to  $n$ -C<sub>110</sub>H<sub>222</sub>. The same procedure is applied concerning data of diamagnetism of  $n$ -alkanes up to  $n$ -C<sub>30</sub>H<sub>62</sub>.

## 1. Introduction

The thermodynamic properties of the hydrocarbons are considered first, as they are the grounds on which the properties of other organic compounds can be correlated. In a generic sense, the hydrocarbons are the root compounds from which all other organic compounds are derived. Indeed, thermodynamical data have been collected for decades on many occasions [1]. However, this work is very fastidious and tedious, and is strongly disregarded nowadays although experimental chemists still have an interest in obtaining such data. Hence, due to the high quality of calculations, most of thermodynamical data are accessible for light molecules by computational chemistry with a high accuracy [2].

Previously, we have observed a perfect linear relationship between ab-initio computations of absolute enthalpies and experimental data of heats of combustion ( $n$  (number of carbon atoms) = 1–20) [3]. Consequently, we have proposed linear relationships to improve the calculated combustion enthalpies up to C<sub>60</sub>H<sub>122</sub>. In this contribution, we have calculated the heat of combustion, the enthalpy of formation, the entropy and the absolute free energies of  $n$ -alkanes up to C<sub>110</sub>H<sub>222</sub> (in the most elongated conformation). We discussed the variations of values for the increment  $\Delta G_n = G_n/n - G_{(n-1)}/(n-1)$  and discussed the difference of data (including bond energies and diamagnetism) between a methyl or a methylene group.

In summary, from ab-initio computations at different levels of theory, our empirical approach is developed in 4 steps:

- 1° check the linearity of experimental results vs number of carbon atoms ( $n = 1-20$ ).
- 2° check the linearity of ab-initio computations vs number of carbon atoms ( $n = 1-110$ ).
- 3° develop a linear relationship between experimental results vs ab-initio computations in order to determine the scaling factor.
- 4° apply scaling factors for an extrapolation from ab-initio computations up to  $n$ -C<sub>110</sub>H<sub>222</sub>.

## 2. Methods

All computations were performed with the *Gaussian 16*, revision A.03, suites of program [4]. The gas-phase geometries of all  $n$ -alkanes were optimized for the most elongated conformation by calculations using the density functional theory method B3LYP [5] with the 6-311++G(d,p) basis set and then refined with the 6-311++G(3df,3pd) basis set or, generally, with the TPSS-TPSS/6.311++G(d,p) basis set [6] level of theory.

A vibrational analysis was performed at the same level of theory in order to determine the zero-point vibrational energy (ZPE), the free energy (not scaled) and to characterize each stationary point as a minimum (number of imaging frequencies,  $N(\text{Imag}) = 0$ ). The total energies,  $E$ , were evaluated at 0 K and the free energies,  $G$ , at 298.15 K. Calculations were performed in ideal gas. These results are listed in the Electronic [Supporting Information](#).

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### 3. Enthalpy of combustion $\Delta H_c^0$ (exp) of $n$ -Alkanes

Experimental values for enthalpy of combustion  $\Delta H_c^0$ (exp) have been determined for  $n = 1$  to 20 [1,7].  $\Delta H_c^0$ (exp) represents the heat evolved in the combustion of the selected hydrocarbon in gaseous oxygen to form gaseous carbon dioxide and liquid water, at 25° C and constant pressure of 1 atm. A perfect linear relationship (1) is observed between  $\Delta H_c^0$ (exp) and the number of carbon atoms  $n$  (ESI Fig. 1).

$$\Delta H_{c,n}^0(\text{exp}) = An + B = -157.472n - 57.51 \text{ (kcal mol}^{-1}, n = 1 - 20, R = 1) \quad (1)$$

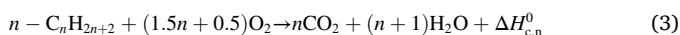
A power law relationship (2) (ESI Fig. 2) is observed concerning the increment  $\delta\Delta H_c^0$ (exp) =  $\Delta H_c^0$ (exp)/ $n - \Delta H_c^0$ (exp)/( $n - 1$ ) which describes the systematic decreasing of enthalpy of combustion with respect to the extension of the chain length [8].

$$\delta\Delta H_{c,n}^0(\text{exp}) = \Delta H_{c,n}^0 / n - \Delta H_{c,n-1}^0 / (n - 1) = 106.32 / n^{2.204} \text{ kcal mol}^{-1}, n = 1 - 20, R = 0.99947 \quad (2)$$

Two procedures can be developed to access to the enthalpy of combustion:

3a. Quantum computations of absolute enthalpy of  $n$ -alkanes  $\Delta H_n$ (comp) and establishing a linear relationship with experimental data ( $n = 1-20$ ).

3b. Quantum computations of enthalpy of the combustion reaction (3) and establishing a linear relationship with experimental data ( $n = 1-20$ ) [9].



3a. Quantum computations of absolute enthalpy of  $n$ -alkanes  $\Delta H_n$ (comp) up to  $n$ -C<sub>110</sub>H<sub>222</sub>.

A perfect linear relationship (4) between  $\Delta H_n$ (comp) and the number  $n$  of carbon atoms in the molecule is observed at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas. (ESI Fig. 3).

$$\Delta H_n(\text{comp}) = -24661.40n - 744.52 \text{ (kcal mol}^{-1}, n = 1 - 110, R = 1) \quad (4)$$

As expected, a perfect linear relationship (5) (ESI Figure 4) was obtained between  $\Delta H_n$ (comp) at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas and experimental data of enthalpy of combustion  $\Delta H_{c,n}^0$ (exp) [7] (methane ruled out).

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_n(\text{calcd}) = 0.0063838\Delta H_n(\text{comp}) - 53.30 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (5)$$

From the relationship (5) an extrapolation up to  $n$ -C<sub>110</sub>H<sub>222</sub>, gives rise to  $\Delta H_{c,n}^0$ (calcd) (6) (Table 2, ESI Fig. 5 and ESI Table 1).

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_{c,n}^0(\text{calcd}) = An + B = -157.43n - 58.05 \text{ (kcal mol}^{-1}, n = 1 - 110, R = 1) \quad (6)$$

For the relation (6), the incremental value per CH<sub>2</sub> (157.43 kcal mol<sup>-1</sup>) is very similar to that proposed earlier by Prosen and Rossini (157.443 kcal mol<sup>-1</sup>) [7]. The value of B is in accordance with the difference between experimental values of heat of combustion of cyclohexane [10] (the 6-membered ring is nearly strainless) [11] ( $\Delta H_c^0 = 936.88 \text{ kcal mol}^{-1}$ ;  $936.88/6 = 156.15 \text{ kcal mol}^{-1}$ ) and  $n$ -hexane [7] ( $\Delta H_c^0 = 995.01 \text{ kcal mol}^{-1}$ ):  $\delta\Delta H_c^0 = 58.13 \text{ kcal mol}^{-1}$ ).

**Table 1**

Calculated values of diamagnetic susceptibility  $\chi_{m,n}$  of  $n$ -alkanes according to relation (29).

$n$	Alkanes	C—C $\chi =$ $-2.90.10^{-6}$ $\text{cm}^3 \text{ mol}^{-1}$	C—H $\chi =$ $-4.25.10^{-6}$ $\text{cm}^3 \text{ mol}^{-1}$	$\chi_m/10^{-6}$ $\text{cm}^3$ $\text{mol}^{-1}$	Exp. $\chi_m/10^{-6}$ $\text{cm}^3$ $\text{mol}^{-1}$ [20]	Calcd $\chi_m/10^{-6}$ $\text{cm}^3$ $\text{mol}^{-1}$
1	CH <sub>4</sub>	–	–17.0	–17.0	–17.4	–16.17
2	C <sub>2</sub> H <sub>6</sub>	–2.90	–25.5	–28.4	–26.8	–27.66
3	C <sub>3</sub> H <sub>8</sub>	–5.80	–34.0	–39.8	–38.6	–39.14
4	C <sub>4</sub> H <sub>10</sub>	–8.7	–42.5	–51.2	–50.3	–50.63
5	C <sub>5</sub> H <sub>12</sub>	–11.6	–51.0	–62.6	–61.5	–62.11
6	C <sub>6</sub> H <sub>14</sub>	–14.5	–59.5	–74.0	–74.1	–73.59
7	C <sub>7</sub> H <sub>16</sub>	–17.4	–68.0	–85.4	–85.2	–85.08
8	C <sub>8</sub> H <sub>18</sub>	–20.3	–76.52	–96.8	–96.6	–96.56
9	C <sub>9</sub> H <sub>20</sub>	–23.2	–85.0	–108.2	–108.1	–108.05
10	C <sub>10</sub> H <sub>22</sub>	–26.1	–93.5	–119.6	–119.5	–119.53
11	C <sub>11</sub> H <sub>24</sub>	–29.0	–102.0	–131.0	–131.8	–131.01
12	C <sub>12</sub> H <sub>26</sub>	–31.9	–110.5	–142.4	–	–142.50
13	C <sub>13</sub> H <sub>28</sub>	–34.8	–119.0	–153.8	–153.7	–153.98
14	C <sub>14</sub> H <sub>30</sub>	–37.7	–127.5	–165.2	–166.2	–165.47
15	C <sub>15</sub> H <sub>32</sub>	–40.6	–136.0	–176.6	–	–176.95
16	C <sub>16</sub> H <sub>34</sub>	–43.5	–144.5	–188.0	–187.6	–188.43
17	C <sub>17</sub> H <sub>36</sub>	–46.4	–153.0	–199.4	–	–199.92
18	C <sub>18</sub> H <sub>38</sub>	–49.3	–161.5	–210.8	–	–211.40
19	C <sub>19</sub> H <sub>40</sub>	–52.2	–170.0	–222.2	–	–222.89
20	C <sub>20</sub> H <sub>42</sub>	–55.1	–178.5	–233.6	–	–234.37
21	C <sub>21</sub> H <sub>44</sub>	–58.0	–187.0	–245.0	–	–245.85
22	C <sub>22</sub> H <sub>46</sub>	–60.9	–195.5	–256.4	–	–257.34
23	C <sub>23</sub> H <sub>48</sub>	–63.8	–204.0	–267.8	–	–268.82
24	C <sub>24</sub> H <sub>50</sub>	–66.7	–212.5	–279.2	–	–280.31
25	C <sub>25</sub> H <sub>52</sub>	–69.6	–221.0	–290.6	–	–291.79
26	C <sub>26</sub> H <sub>54</sub>	–72.5	–229.5	–302.0	–	–303.27
27	C <sub>27</sub> H <sub>56</sub>	–75.4	–238.0	–313.4	–	–314.76
28	C <sub>28</sub> H <sub>58</sub>	–78.3	–246.5	–324.8	–	–326.24
29	C <sub>29</sub> H <sub>60</sub>	–81.2	–255.0	–336.2	–	–337.73
30	C <sub>30</sub> H <sub>62</sub>	–84.1	–263.5	–347.6	–	–349.21

The linear relationship (7) (ESI Figure 6) obtained between  $\Delta H_n$ (comp) and experimental data of enthalpy of combustion  $\Delta H_c^0$ (exp) [7] including methane ( $n = 1-20$ ) (at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas) led to values with a larger discrepancy for the difference  $\Delta H_c^0$ (exp) –  $\Delta H_n$ (calcd) (mean value for the difference according to the relation 5:  $\pm 0.138$ , to the relation 7:  $\pm 0.313 \text{ kcal mol}^{-1}$ ) (ESI Table 2).

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_n(\text{calcd}) = 0.006385\Delta H_n(\text{comp}) - 52.76 \text{ (kcal mol}^{-1}, n = 1 - 20, R = 1) \quad (7)$$

Computations of the absolute enthalpy with a larger basis set at the B3LYP/6-311G++(3df,3pd) level of theory provided results (relationships 8 and 9) with a similar accuracy for the linear relationship and, in this case also, methane should be ruled out (ESI Figures 7, 8 and ESI Table 3).

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_n(\text{calcd}) = 0.006384\Delta H_n(\text{comp}) - 53.29 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (8)$$

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_n(\text{calcd}) = 0.006386\Delta H_n(\text{comp}) - 52.76 \text{ (kcal mol}^{-1})(n = 1 - 20, R = 1) \quad (9)$$

Mean value for the difference  $\Delta H_c^0$ (exp) –  $\Delta H_n$ (calcd) according to the relation 8:  $\pm 0.1$ , to the relation 9:  $\pm 0.2 \text{ kcal mol}^{-1}$ ) (ESI Table 2).

3b. Calculated enthalpy of combustion of linear alkanes  $\Delta H_n$ (calcd) at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas according to the combustion reaction (3).



A perfect linear relationship (10) is observed between  $\Delta H_c^\circ(n(\text{comb}))$  and  $\Delta H_c^\circ(n(\text{exp}))$  at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas (methane ruled out) (ESI Figure 9, and ESI Table 4). Mean value for the difference  $\Delta H_c^\circ(n(\text{exp})) - \Delta H_n(\text{calcd})$  according to the relation 10:  $\pm 0.06 \text{ kcal mol}^{-1}$ .

$$\Delta H_{c,n}^0(\text{exp}) \sim \Delta H_n(\text{calcd}) = 1.181195 \Delta H_{c,n}^0(\text{comb}) - 17.13 \text{ (kcal mol}^{-1})(n = 2 - 20, R = 1) \quad (10)$$

In the ESI Table 5, we compare the enthalpy of combustion of  $n$ -alkanes  $\Delta H_n(\text{calcd})$  at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas according to the combustion reaction (3) (relationship (10)) and results of the relation (5) and we were pleased to find identical results according to the used method.

As previously mentioned [3], the enthalpy of combustion of hydrocarbon unit  $\Delta H_c^\circ/n$  decreases according to the chain length of  $n$ -alkanes (ESI Table 6, ESI Figure 10). The decrease of stability ( $\delta \Delta H_c^\circ/n(\text{calcd})/n = 54.84 \text{ kcal mol}^{-1}$ ,  $n = 1-110$ , Eq. (11)) is due to the lower C–C bond energies in comparison with the C–H bond (See section 7). For the heat of combustion of 1 g of  $n$ -alkane, the difference reaches  $\sim 2 \text{ kcal mol}^{-1}$  from methane to  $\text{C}_{35}\text{H}_{72}$ . Heat generated in combustion reactions, when converted into a vectored force, provides the dynamics for thermodynamics [12].

$$\Delta H_c^0(\text{C}_{110}\text{H}_{220})/110 - \Delta H_c^0(\text{CH}_4) = 54.84 \text{ kcal mol}^{-1} \quad (11)$$

#### 4. Enthalpy of formation of $n$ -alkanes

A perfect linear relationship (12) between experimental data for the enthalpy of formation  $\Delta H_f^\circ(n(\text{exp}))$  [1] and the number of carbon atoms  $n$  is observed (methane ruled out)(ESI Fig. 11 and ESI Table 7).

$$\Delta H_{f,n}^0(\text{exp}) = -4.9317n - 10.326 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (12)$$

Similarly, the perfect linear relationship (13) is observed between  $\Delta H_n(\text{comp})$  and experimental data of heats of formation  $\Delta H_f^\circ(n(\text{exp}))$  for  $n = 2-20$  (methane ruled out) at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas (ESI Figure 12).

$$\Delta H_{f,n}^0(\text{exp}) \sim \Delta H_{f,n}^0(\text{calcd}) = 0.00020 \Delta H_n(\text{comp}) - 10.177 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (13)$$

Mean value for the difference  $\Delta H_c^\circ(n(\text{exp})) - \Delta H_n(\text{calcd})$  according to the relation 13:  $\pm 0.04 \text{ kcal mol}^{-1}$  (ESI Table 7, and ESI Fig. 13). From the relationship (12), an extrapolation up to  $n\text{-C}_{110}\text{H}_{222}$ , gives rise to  $\Delta H_f^\circ(n(\text{calcd}))$  (Table 2, Eq. (14), ESI Table 7, and ESI Fig. 13) [13].

$$\Delta H_{f,n}^0(\text{calcd}) = -4.93228n - 10.33 \text{ (kcal mol}^{-1}, n = 1 - 110, R = 1) \quad (14)$$

#### 5. Entropy of $n$ -alkanes

Again, a perfect linear relationship (15) between experimental data for the entropy  $S_n^\circ(\text{exp})$  [1] and the number of carbon atoms  $n$  is observed (ESI Fig. 14 and ESI Table 8) at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas.

$$S_n^\circ(\text{exp}) = 9.3563n + 36.4 \text{ (cal mol}^{-1} \text{ K}^{-1}, 298.15 \text{ K}, n = 1 - 20, R = 1) \quad (15)$$

As reported for enthalpies (*vide supra*), a perfect linear relationship (16) (ESI Figure 15) is observed between  $S_n^\circ(\text{comp})$  and experimental data [1] of entropy  $S_n^\circ(\text{exp})$  for  $n = 2-20$  (methane ruled out) at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas (ESI Table 8) followed by an extrapolation for  $n = 21$  to 110 (Table 2).

$$\begin{aligned} S_n^\circ(\text{exp}) &\sim \Delta H_n(\text{calcd}) \\ &= 1.192386 S_n^\circ(\text{comp}) - 13.77 \text{ (cal mol}^{-1} \text{ K}^{-1}, 298.15 \text{ K}, n \\ &= 2 - 20, R = 1) \end{aligned} \quad (16)$$

In the ESI Table 9, the comparison between  $S_n^\circ(\text{exp})$  [1] and  $S_n^\circ(\text{calcd})$  according to the relationship (16) shows a very weak difference ( $\pm 0.12 \text{ cal mol}^{-1} \text{ K}^{-1}$ , ( $>0.2\%$ , except methane).

ESI Figure 16 confirms the linear relationship (17) between calculated entropy on  $n$ -alkanes  $S_n^\circ(\text{calcd})$  and the number  $n$  of carbon atoms in the molecule of  $n$ -alkanes at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas.

$$S_n^\circ(\text{calcd}) = 7.755358n + 43.72 \text{ (cal mol}^{-1} \text{ K}^{-1}, 298.15 \text{ K}, n = 1 - 110, R = 1) \quad (17)$$

Computations (ESI Table 10) of the entropy  $S_n^\circ(\text{comp})$  with a larger basis set at the B3LYP/6-311G++(3df,3pd) level of theory afforded values of  $S^\circ(\text{calc})$  with a comparable accuracy from the linear relationship (18) (ESI Fig. 17 and ESI Table 11) but, in this case also, methane should be ruled out.

$$S_n^\circ(\text{exp}) = 1.26191 S_n^\circ(\text{comp}) - 18.55 \text{ (cal mol}^{-1} \text{ K}^{-1}, 298.15 \text{ K}, n = 2 - 20, R = 1) \quad (18)$$

#### 6. Free energy of $n$ -alkanes

Plot (19) between experimental data  $G_n^\circ(\text{exp})$  [1] and the number  $n$  of carbon atoms showed a deviation from linearity for the methane (ESI Figure 18).

$$G_n^\circ(\text{exp}) = 2.027n - 12.35 \text{ (kcal mol}^{-1}, n = 1 - 20, R = 0.9992) \quad (19)$$

Consequently, we have ruled out the value of the methane in the linear relationship (20) between  $G_n(\text{exp})$  and the number of carbon atoms  $n$  (ESI Fig. 19).

$$G_n^\circ(\text{exp}) = 2.00n - 11.945 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (20)$$

Then computations of  $G_n^\circ(\text{comp})$  for  $n$ -alkanes at the TPSS-TPSS/6-311++G(d,p) level of theory in ideal gas led to the linear relationship (21) (ESI Fig. 20).

$$G_n^\circ(\text{comp}) = An + B = -24663.72n - 757.55 \text{ (kcal mol}^{-1}, n = 1 - 110, R = 1) \quad (21)$$

The value of A corresponds to the computed free energy per methylene group and the value of B results of the presence of the two C–H bonds of the end methyl groups (computed free energy of cyclohexane:  $\Delta G^\circ = 147\,991.89 \text{ kcal mol}^{-1}$ ;  $147\,991.89/6 = 24\,665.31 \text{ kcal mol}^{-1}/\text{CH}_2$ ;  $n$ -hexane:  $\Delta G^\circ = 148\,739.55 \text{ kcal mol}^{-1}$ ;  $\delta \Delta G^\circ = 747.65 \text{ kcal mol}^{-1}$ ).

Then, a perfect linear relationship (22) is observed between  $G_n^\circ(\text{comp})$  and  $G_n^\circ(\text{exp})$  (ESI Figure 21).

$$G_n^\circ(\text{exp}) \sim G_n(\text{calcd}) = -0.00008095 G_n^\circ(\text{comp}) - 12.02 \text{ (kcal mol}^{-1}, n = 2 - 20, R = 1) \quad (22)$$

From the relationship (22), an extrapolation up to  $n\text{-C}_{110}\text{H}_{222}$ , gives rise to  $\Delta G_n^\circ(\text{calcd})$  (Table 2, ESI Table 12 and ESI Figure 22, relationships (23–25)).

$$G_n/n - G_{(n-1)}/(n-1) = -757.55/n(n-1) \text{ kcal mol}^{-1} \quad (23)$$

$$G_n[\text{C}_n\text{H}_{(2n+2)}]/n - G_n[\text{C}_{(n-1)}\text{H}_{2n}]/(n-1) = 1064.09/n^{2.08} \text{ kcal mol}^{-1} \quad (24)$$

$$\text{Log}\delta G_n = -2.0793 \text{ Log } n + 3.026 \quad R = 0.99935 \quad (25)$$

From the relation (21), we analyzed in the Table S-13, the difference between the free energy of two consecutive units  $G_n/n - G_{(n-1)}/(n-1) = -757.55/n(n-1) \text{ kcal mol}^{-1}$  (ESI Figures 23 and 24) [14].

## 7. Bond energies of *n*-alkanes

As previously mentioned [3], the enthalpy of combustion of hydrocarbon unit  $\Delta H_c^\circ/n$  decreases according to the chain length of *n*-alkanes (ESI Table 6, ESI Figure 11). The decrease of stability ( $\delta\Delta H_c^\circ/n(\text{calcd})/n = 54.84 \text{ kcal mol}^{-1}$ ,  $n = 1-110$ ) is due to the lower C—C bond energies in comparison with the C—H bond energies as displayed in Eq. (26) [15].

$$E_{(\text{C}-\text{C})} = 87.0; E_{(\text{C}-\text{H} \text{ methane})} = 105.0; E_{(\text{C}-\text{H} \text{ primary})} = 100.7; E_{(\text{C}-\text{H} \text{ secondary})} = 99.0 \text{ kcal mol}^{-1};$$

$$E_n = (n-1)E_{(\text{C}-\text{C})} + 6E_{(\text{C}-\text{H} \text{ prim.})} + (n-2)E_{(\text{C}-\text{H} \text{ second.})} \\ = (n-1)87.0 + 6 \times 100.7 + (n-2)198.0 = 285.0n + 121.2 \text{ kcal mol}^{-1} \quad (26)$$

From the relation 26 (ESI Table 14 and ESI Fig. 25, 26 and 27), 285.0 corresponds to the contribution of one methylene group ( $87 + 2 \times 99 \text{ kcal mol}^{-1}$ ) and 121.2 to the two hydrogen atoms brought by the end methyl groups (bond energies  $E_n$  for the cyclohexane: 1710.0, hexane: 1831.2 affording  $\delta E = 121.2 \text{ kcal mol}^{-1}$ ).

## 8. Diamagnetic susceptibilities $\chi$ of *n*-alkanes

The classical work of Pascal [16] has established that the isotropic diamagnetic susceptibilities of molecules,  $\chi_m$ , (the ability of a substance to be repelled by an external magnetic field ( $\chi < 0$ )) can be approximated by simple addition of atomic or bond susceptibilities (Pascal's constants) [17]. Since, it was found a correlation between C—H bond contributions and the bond lengths, [18] and predicting values from group contributions [19]. Diamagnetic susceptibilities  $\chi$  are temperature independent.

The susceptibility magnetic  $\chi$ , is measured by the ratio  $\kappa$  of the intensity of magnetization produced  $M$  in a substance to the magnetizing force or intensity of field  $H$  to which it is subjected:  $M = \kappa H$  ( $\kappa$  is dimensionless), then the molar susceptibility is defined by  $\chi_m = \kappa V_m$  ( $V_m$  = molar volume). In cgs system, the customary unit for  $\chi_m$  is  $\text{cm}^3 \text{ mol}^{-1}$ .

A perfect linear relationship (28) is observed between the experimental diamagnetism values [20] and the number  $n$  of carbon atoms in the molecules of *n*-alkanes (ESI Table 15 and ESI Fig. 27).

$$\chi_m = -11.48n - 4.69 \quad (10^{-6} \text{ cm}^3 \text{ mol}^{-1}, n = 1 - 11, 13, 14, 16, R = 1) \quad (28)$$

The regression equation 28 indicates that each  $\text{CH}_2$  group contributes  $-11.48$  to the diamagnetic susceptibility ( $\chi_{\text{C-H}} = -4.25 \cdot 10^{-6}$ ,  $\chi_{\text{C-C}} = -2.9 \cdot 10^{-6}$ ) [16d,16e]. The constant  $-4.69$  represents the contribution of the two hydrogen atoms at the ends of the carbon chain. This value is not too far off from the measured susceptibility of liquid hydrogen  $\text{H}_2$  of  $-5.44 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .

From the relationship (28), an extrapolation up to  $n\text{-C}_{30}\text{H}_{62}$ , gives rise to  $\chi_{m,n}(\text{calcd})$  (relationship 29)(Table 1, ESI Table 15 and ESI Figure 28).

$$\chi_{m,n}(\text{calcd}) = -11.484n - 4.69 \quad (10^{-6} \text{ cm}^3 \text{ mol}^{-1}, n = 1 - 30, R = 1) \quad (29)$$

## 9. Conclusion

The realization that the molecular value of some property could be obtained as a sum of group contributions arose not long after the introduction of structural formulas into chemistry [7,21,22].

From experimental data or quantum-chemical calculations

concerning *n*-alkanes, an astonishing linearity of results is observed. Nevertheless, often methane should be ruled out and it appears as a particular alkane. In contrast, magnetic properties are perfectly linear with the number of carbon atoms.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRedit authorship contribution statement

**G erard Audran:** Validation. **Jean-Patrick Joly:** Validation. **Sylvain R.A. Marque:** Validation. **Didier Siri:** Software. **Maurice Santelli:** Conceptualization, Methodology, Writing – original draft.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.comptc.2022.113770>.

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