Atom–bond connectivity and the energetic of branched alkanes

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ARTICLE INFO

ABSTRACT

Here we introduce a new topological approach which provides a good model for the stability of linear and branched alkanes as well as the strain energy of cycloalkanes. We find that the ratio of 1,3-interactions with respect to the total number of 1,2-, 1,3- and 1,4-interactions plays a fundamental stabilizing role in the energetic of alkanes. These stabilizing effects are larger in branched than in linear alkanes. The heat of formation of alkanes can be obtained as a combination of stabilizing effects coming from atoms, bonds and protobranches.

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In 1998, Estrada et al. [1] defined a new topological index that displays an excellent correlation with the heat of formation of alkanes. This index, named ABC (atom–bond connectivity) is defined using a modification of the Randić graph-theoretic invariant [2]. The ABC index is defined as follows [1]:

$$\text{ABC}(G) = \sum_{r=1}^{m} \left(\frac{\varepsilon_{ij}}{\delta_i \delta_j} \right)_r^{0.5} = \sum_{r=1}^{m} \left(\frac{\delta_i + \delta_{j-2}}{\delta_i \delta_j} \right)_r^{0.5}, \tag{1}$$

where δ_i is the degree of the ith vertex, ε_{ij} is the degree of the edge formed by the nodes i and j and the summation is carried out over all bonds of the alkane. As most of topological indices the ABC index is based on hydrogen-depleted graphs. The introduction of graph-theoretic concepts in chemistry is well known and the reader is referred to the following references for definitions and notations [3,4].

Topological indices are criticized in certain circles of chemical research where they are considered as 'simplistic' models of the chemical structure lacking a physical meaning [5]. On the other hand, alkanes are the simplest organic molecules and the use of topological indices for studying alkanes has been the focus of many of the before mentioned criticisms. However, understanding the structure and energetic of alkanes is necessary to understand more complex molecules [6]. As an example we focus here on a controversy arisen in trying to explain the causes for the stabilization effects in branched alkanes, which is discussed in the next paragraphs.

It is known that branched alkanes are more stable than their straight chain isomers. Two recent papers in leading chemical journals assign contradictory causes for stabilization effects in branched alkanes. Gronert [7,8] has suggested that 'geminal repulsion' provides a conceptual framework for explaining the stability differences of alkanes. Geminal repulsion refers to the repulsive interactions of atoms separated by two bonds, i.e., 1,3-interactions. Schleyer et al. [9,10] claim that 1,3-interactions produce stabilization of branched alkanes and in a lower degree also of linear ones. Geminal repulsion can be understood as a steric interaction determined by the geometry of the molecule. In contrast, protobranching appears to be produced by electron correlation [9–12].

The aim of the current work is to develop an approach on the basis of the ABC index which explains the before mentioned differences in the energetic of linear and branched alkanes both qualitatively and quantitatively. Our approach is basically a topological one. By topological we mean those characteristics which depend directly on the connectivity of atoms and bonds. The study of topological effects has been primordial in understanding the structure of conjugated hydrocarbons, their aromaticity and properties derived from it as well as in the study of solid state physics [13–16]. Then we investigate here the role played by the topological molecular factors on the stability of alkanes.

The use of the hydrogen-depleted graphs in order to represent alkanes can be understood in terms of an approach introduced by Franklin [17], in which each carbon atom and its associated hydrogens are treated as a united atom. In this approach methane is isoelectronic to neon, ethane is isoelectronic to F_2, propane to FOF, isobutane to NF_3, neopentane to CF_4, etc. [17]. Then the united-atom approach is equivalent to the use of the so-called 'hydrogen-depleted graphs'. For the sake of brevity hereafter we will refer to united-atoms as 'carbon' atoms.

The next step in the current approach is to find a connection between the ABC invariant and certain structural parameters that could be involved in the stabilization of branched alkanes. Let us consider 1,2-, 1,3- and 1,4-interactions between the united atoms in an alkane. Here the nature of the interactions does not matter but only the number of united-atoms interacting to each other. The differentiation between the different types of groups in alkanes, e.g., CH_3, CH_2, CH and C, is accounted for through the use of the degree of the corresponding vertex in the hydrogen-depleted

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graph. For instance, a vertex of degree 1 represents a CH_3 group, a vertex of degree 2 represents a CH_2 group and so forth.

In the expression (1) the term $\delta_i + \delta_j - 2$ represents the degree of the bond formed by the atoms i and j, which is the number of bonds incident to the atoms i or j. In other words, this term represents the number of 1,3-interactions involving the i, j bond. Let us take for instance the C–C bond of 2,2,3,3-tetramethylbutane. The degree of this bond is 6, which represents the six interactions between CH_3 groups and the C separated by two bonds. On the other hand, the term $\delta_i \delta_j$ counts the number of 1,2-, 1,3- and 1,4-interactions involving the i, j bond. For instance, in the before mentioned example $\delta_i \delta_j = 16$, which counts the C–C interaction, six CH_3–C–C interactions and nine CH_3–C–C–CH_3 interactions. Thus, the term $\frac{\delta_i + \delta_j - 2}{\delta_i \delta_j}$ represents the ratio of 1,3-interactions to the total number of 1,2, 1,3 and 1,4-interactions. In the previous example the ratio of 1,3-interactions accounted by the C–C bond is 3/8 (37.5%).

Now, in order to put the current approach in the context of the main stream of molecular approaches, we consider the term inside the bracket of the ABC invariant as an interatomic potential function V_{ij}

$$V_{ij} = \left(\frac{g}{b+g+l} \right)^\alpha = \left(\frac{k_i + k_j - 2}{k_i k_j} \right)^\alpha, \tag{2}$$

where b, g and l account for the number of (bond) 1,2-, (geminal) 1,3- and (long-range) 1,4-interactions and α is an adjustable parameter. Then, we obtain the discrete values of the energies ε of alkanes by solving the secular equations using a tight-binding, Hückel-like, approach

$$\sum_{r=1}^{n} c_{jr}[H_{jr} - pS_{jr}] = 0, j = 1, \dots n, \tag{3}$$

where the coefficients $c_j(a)$ arise from the linear combination of united-atom orbitals, ϕ_r, centered at the united-atom a to give molecular orbitals

$$\psi_j = \sum_{b=1}^{n} c_j(a)\phi_r. \tag{4}$$

The summations in (3) and (4) are taken over all n atoms. The terms H_{jr} in (3) are the entries of the matrix $\mathbf{H}$ and ε_j correspond to the values of the energies for the molecular orbitals. The nontrivial solutions of Eq. (3) are obtained by solving the determinant equation

$$|\mathbf{H} - \varepsilon \mathbf{S}| = 0. \tag{5}$$

We assume that the Coulomb integral $\mathbf{H}_{ii}$ of an orbital ϕ_i is equal to p for all the carbon atoms in alkanes, $H_{ii} = p$. The resonance integral $\mathbf{H}_{ij}$ between orbitals ϕ_i and ϕ_j is assumed to be zero, unless i and j are adjacent carbon atoms, in which case it is taken to be $H_{ij} = -qV_{ij}$, where V_{ij} is the previously introduced potential function. We consider that the orbitals are orthonormal, thus $S_{ij} = \delta_{ij}$. Then if we divide every entry of the secular determinant by q the secular determinant for an alkane having n carbon atoms is written as

$$\begin{vmatrix} \lambda & -\delta_{1,2}V_{12} & -\delta_{1,3}V_{13} & \cdots & -\delta_{1,n}V_{1n} \\ -\delta_{2,1}V_{21} & \lambda & -\delta_{2,3}V_{23} & \cdots & -\delta_{2,n}V_{2n} \\ -\delta_{3,1}V_{31} & -\delta_{3,2}V_{32} & \lambda & \cdots & -\delta_{3,n}V_{3n} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ -\delta_{n,1}V_{n1} & -\delta_{n,2}V_{n2} & -\delta_{n,3}V_{n3} & \cdots & \lambda \end{vmatrix} = 0, \tag{6}$$

where δ_{ij} is a Dirac function taking the value of one if the two atoms are bonded or zero otherwise, and $\lambda_j = \frac{p - E_j}{q}$ are the eigenvalues of the matrix $\mathbf{H}$. From now on we set $p = 0$ without loss of generality, since p simply sets the origin of the energy scale and we assumed $q < 0$.

In addition, we define an electronic partition function to characterize the structure of an alkane

$$Z = \sum_{j=1}^{n} e^{-\beta \varepsilon_j} = \sum_{j=1}^{n} e_j^{-\beta|q|\lambda}, \tag{7}$$

where $\beta = 1/kT$ is the inverse temperature (T) and k is the Boltzmann constant [18]. Hereafter we set $|q|\beta \equiv 1$ for simplicity, since $|q|$ specifies an energy scale chosen arbitrarily. Then, the partition function (7) is determined by the eigenvalues of the adjacency matrix of the hydrogen-depleted graph. Note that for bipartite graphs, such as alkanes, the partition function (7) is identical to the Estrada index of the graph [19–22].

To start with we select the series of linear and branched alkanes studied by Gronert with the exception of methane [7,8]. We calculate the partition function previously defined for these alkanes using the values of $\alpha = 1/2, 1/3, 1, 2, 3$. We observe that the best results are obtained for the partition function calculated with $\alpha = 2$, which shows excellent correlation with the experimental values of the heat of formation of alkanes (correlation coefficient, $r = 0.9996$) (see Table 1),

$$\Delta H_f = -10.7456 - 4.6308Z. \tag{8}$$

Gronert [7] obtained for the same set of alkanes a correlation coefficient $r = 0.9996$ using a six-parameter model. The intercept of the model (8) is simply interpreted as the effect of the two terminal CH_3 groups present in every alkane. From the experimental value of ΔH_f of ethane we can see that each CH_3 contributes with -10.0 kcal/mol, which coincides very well with the intercept of the model (8). As a further test we calculate ΔH_f for cyclohexane, which neither have any terminal CH_3 nor any strain energy. Then we make the calculation using simply $\Delta H_f = -4.6308Z$, which gives a value of $\Delta H_f = -29.55$ kcal/mol, very close to the experimental value of $\Delta H_f = -29.4$ kcal/mol.

Using the simplified Eq. $\Delta H_f = -4.6308Z$ we calculate ΔH_f for cycloalkanes, which are shown in Table 2 together with their strain energy E_{strain} [23].

In general the model obtained for calculating ΔH_f of alkanes can be extended to any polycycloalkane by using the cyclomatic number, $\gamma = m - n + 1$, where m is the number of C–C bonds and n is the number of carbon atoms. Then,

$$\Delta H_f = 10.7456(\gamma - 1) - 4.6308Z. \tag{9}$$

For instance, the values of E_{strain} calculated (experimental values in parentheses) for bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane are 60.9 kcal/mol (63.9 kcal/mol) and 51.8 kcal/mol

Table 1
Partition function as well as the calculated and experimental heat of formation of alkanes studied by Gronert [7,8]

Compound	Z	ΔH_f	Calcd. ΔH_f	Error
Ethane	2.0000	−20.0	−20.0	0.0
Propane	3.1263	−25.2	−25.0	0.2
Butane	4.1898	−30.1	−30.4	−0.3
Isobutene	4.6226	−32.2	−32.1	0.1
Pentane	5.2533	−35.1	−35.1	0.0
Isopentane	5.5389	−36.4	−36.7	−0.2
Neopentane	6.4049	−40.4	−40.1	0.1
Hexane	6.3168	−40.0	−40.0	0.0

Table 2
Partition function, calculated and experimental heat of formation as well as experimental and calculated strain energies of the cycloalkanes studied here

Compound	Z	ΔH_f	Calcd. ΔH_f	E_{strain}	Calcd. E_{strain}
Cyclopropane	3.1746	12.75	−14.70	27.6	27.4
Cyclobutane	4.2553	6.56	−19.70	26.4	26.3
Cyclopentane	5.3173	−18.3	−24.62	6.5	6.3
Cyclohexane	6.3809	−29.4	−29.55	0.0	0.2
Cycloheptane	7.4444	−28.35	−34.47	6.3	6.1
Cyclooctane	8.5079	−30.00	−39.40	9.6	9.4

(54.8 kcal/mol), respectively. For cubane, using $\Delta H_f = 148.7$ kcal/mol we obtain an $E_{strain} = 152.4$ kcal/mol, which compares well with the value of 157.4 kcal/mol reported experimentally.

According to these results, the ratio of 1,3-interactions with respect to the total number of 1,2-, 1,3- and 1,4-interactions appears to be important for the energetic of a bond. Now, let us take a closer look to the potential function used here. Let us consider two hypothetical molecules A and B having the same potential for all bonds excepts for bonds a and b for which $V_{ij}(A) > V_{ij}(B)$. Then, according to the secular determinant (6), the molecule A has lower energy than the molecule B. In other words, A is more stable than molecule B. Consequently, the larger the value of the potential V_{ij} the larger the stability of the corresponding bond. According to expression (2), there are two ways of increasing the value of V_{ij}, i.e., increasing the number of 1,3-interactions or decreasing the number the 1,2- and/or 1,4-interactions. In such a way, the numerator of the potential function and of the ABC index represents attractive (protobranching) interactions and the denominator represents repulsive interactions (geminal repulsion). Clearly, increasing the attractive (numerator) interactions increases the stabilization of the corresponding alkane.

In order to obtain a correspondence between the model (8) and the contributions of atoms, bonds and protobranches, we expand Z in terms of the Hamiltonian matrix [24,25],

$$Z = \mathrm{tr}\,e^{-\beta \mathbf{H}}$$

$$= \mathrm{tr}\left(\mathbf{I} + (-\beta)\mathbf{H} + \frac{(-\beta)^2 \mathbf{H}^2}{2!} + \frac{(-\beta)^3 \mathbf{H}^3}{3!} + \cdots + \frac{(-\beta)^k \mathbf{H}^k}{k!} + \cdots\right).$$

$$(10)$$

We recall that $\mathrm{tr}(\mathbf{A} + \mathbf{B}) = \mathrm{tr}\mathbf{A} + \mathrm{tr}\mathbf{B}$ and that

$$\mathrm{tr}(\mathbf{H}^k) = \sum_{i_1, i_2, \ldots i_k} \mathbf{H}_{i_1 i_2} \mathbf{H}_{i_2 i_3} \cdots \mathbf{H}_{i_k i_1}. \tag{11}$$

Then, every single term in this sum represents a walk starting and ending with the orbital i_1 and visiting only pairs of connected atoms. The weight of such walk is the product of the interaction potentials. Then, the partition function represents a weighted sum of all closed walks of different lengths in the molecule. Every walk is normalized by the factorial of its length. In the case of acyclic molecules, e.g., alkanes, all odd powers of $\mathbf{H}$ are zero and we have

$$Z_{alkane} = n + \frac{1}{2}\mathrm{tr}(\mathbf{H}^2) + \frac{1}{24}\mathrm{tr}(\mathbf{H}^4) + \cdots, \tag{12}$$

where the first term represents the number of carbon atoms n_{atoms}, the second is an energy contribution of bonds $\sum E_{bonds}$ and the third is an energy contribution of pairs of adjacent bonds, which can be interpreted as the contribution coming from the protobranches, $\sum E_{protobranches}$. Then, by substituting (12) into (8), we can obtain a model for calculating the heat of formation of alkanes

$$\Delta H_f \approx -10.7456 - 4.6308 n_{atoms} - 2.3154 \sum E_{bonds}$$
$$- 0.1930 \sum E_{protobranches}, \tag{13}$$

where

$$\sum E_{bonds} = \mathrm{tr}(\mathbf{H}^2) \tag{14}$$
$$\sum E_{protobranches} = \mathrm{tr}(\mathbf{H}^4). \tag{15}$$

The model (13) clearly shows that the effects coming from carbon atoms, bonds and protobranches are all of stabilizing nature. The contribution of the terminal CH_3 groups, which is the intercept of the regression model, is always the same for any alkane. In Fig. 1 we can see the contributions of these terms to ΔH_f of pentane isomers. It can be seen that neopentane has lower heat of formation than isopentane and pentane due to its larger C–C bond and proto-
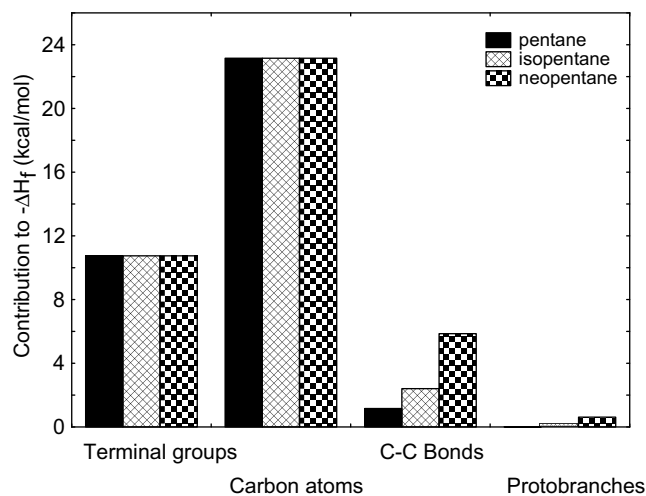

Fig. 1. Contribution of different terms to the stabilization of pentane isomers.

branches' contributions. The bond contribution accounts for about 15% of the total ΔH_f of neopentane and protobranching stabilizing effect accounts for 1.5%.

In Fig. 2 we illustrate the same contributions for 2,3-dimethylpentane and 2,2-dimethylbutane. Despite 2,2-dimethylbutane overtakes 2,3-dimethylpentane in the contributions of bonds and protobranches, the second has lower ΔH_f than the first due to the contribution of carbon atoms, which accounts for 66% of the total ΔH_f. Similar situation is observed for the case of neopentane and 2,3-dimethylbutane (graphic not shown). It is worth mentioning that the values of ΔH_f using the approximated expression (13) are exactly the same as those obtained by model (8).

On the other hand, the diagonal entries of the corresponding powers of $\mathbf{H}$ can be interpreted as the contribution of the corresponding atoms to the different energy types: $(\mathbf{H}^2)_{ii} = E_{bonds}(i)$ and $(\mathbf{H}^4)_{ii} = E_{protobranches}(i)$. In general,

$$(\mathbf{H}^k)_{ii} = \sum_{j=1}^{n} [\phi_j(i)]^2 (\varepsilon_j)^k. \tag{16}$$

By using these expressions in model (13), we can calculate the contribution of every atom to the bond and probranching energies. Accordingly, not all carbon atoms have the same contribu-
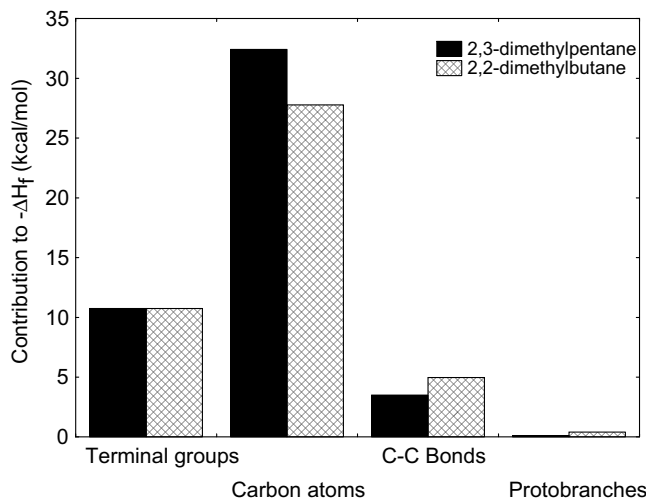

Fig. 2. Contribution of different terms to the stabilization of two branched alkanes of different sizes.

tions to these kinds of energies. Consequently, the assumptions of Gronert [7,8] that 'all C–H bonding interactions' and 'all C–C bonding interactions provide the same stabilization' do not appear to be correct under the current approach. For instance, the contribution of CH_3 to bond and protobranching energies in pentane are 0.0625 and 0.00781, respectively. However, the same contributions in neopentane are 0.3164 and 0.40045, respectively. Observe that in neopentane the contribution of the methyl group to the protobranching is even larger than that to the bond energy.

In summary, we have introduced a new approach based on a Hückel-like Hamiltonian, which provides a good model for explaining the energetic of linear and branched alkanes. It also permits to estimate very precisely the strain energy of cycloalkanes. More importantly, we have found that the proportion of 1,3-interactions with respect to the total number of 1,2-, 1,3- and 1,4-interactions plays a fundamental stabilizing role in the energetic of alkanes. These stabilizing effects are larger in branched alkanes but it is also present in linear ones as advanced by Schleyer et al. [9]. We also found that the contribution of carbon atoms to the stability of alkanes depends very much on their chemical environment. The heat of formation of alkanes can be obtained as a function of stabilizing effects coming from atoms, bonds and protobranches.

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