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Semi-Empirical Calculation of the Energy of Formation of Hydrocarbons and Radicals

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Nous proposons une méthode de calcul de l'énergie d'atomisation ou de formation d'hydrocarbures et de radicaux pouvant contenir à la fois des liaisons simples, doubles et triples, conjuguées ou non. Nous calculons séparément la contribution des électrons π et des électrons σ à l'énergie de liaison. L'énergie de liaison σ est représentée par une somme de termes dont chacun est associé à une liaison de la molécule. L'énergie de liaison π est calculée à l'aide d'une extension de la méthode de Pariser, Parr et Pople. Les résultats du calcul sont en accord satisfaisant avec les données expérimentales.

A method of calculating the energy of formation of hydrocarbons and radicals having at the same time, single, double and triple bonds, conjugated or not, is developed. The π-bond energy and the σ-bond energy are considered independently. The σ-bond energy is represented by a sum of terms, each of which is associated with a bond of the molecule. The π-bond energy is calculated by an extension of the Pariser, Parr and Pople method. The agreement with experimental results is satisfactory.

Es wird eine Methode entwickelt, für konjugierte und nicht konjugierte Kohlenwasserstoffe und Radikale mit einfachen, Doppel- und Dreifachbindungen die Bildungsenergie zu berechnen. Die Anteile der π- und σ-Elektronen an der Bildungsenergie werden getrennt berechnet. Die Bindungsenergie der σ-Elektronen wird durch eine Summe von jeweils mit einer Molekülbindung verknüpften Termen dargestellt, die der π-Elektronen mit einer erweiterten PPP-Theorie. Die Rechenergebnisse stimmen mit den Experimenten gut überein.

Introduction

The purpose of this work is to calculate, by a method as simple and general as possible, the energy of formation of hydrocarbons and radicals, containing carbon atoms in any state of hybridization.

These energies of formation are quantities which are interesting by themselves and their values are useful in many experimental studies.

In this work, we have calculated the atomization energy at 0 °K of hydrocarbons and radicals, i.e. the opposite of their energy of formation from gaseous carbon and hydrogen atoms. The atomization energy is thus equal to the energy necessary to break all the bonds of a molecule. By definition, it is equal to the sum of the "bond energies". The latter entities are not well defined and are utilitarian concepts only. Conventionally, the energy of a bond is the energy necessary to break this bond, in a process in which all the bonds of the molecule are broken simultaneously. This quantity is taken positively; hence the atomization energy is also a positive quantity.

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The bond energies were recently reviewed by SKINNER and PILCHER [28]. The authors discuss the definition, the validity and the utility of this concept, and they critically review the different methods which have been proposed to calculate the atomization energy of molecules from bond and interaction energy terms. A general method, suitable for molecules having at the same time single, double and triple bonds, conjugated or not, is, at the present time, not available.

Very recently, DEWAR and his collaborators [6, 3] have calculated the energy of formation of aromatic hydrocarbons and polyenes. In their method, as in the method we are going to describe, σ-electrons and π-electrons are considered independently. However, the σ-bond energy and the π-bond energy are calculated in a different way.

Description of the Method

If, according to the usual approximation, the π- and σ-electrons are considered independently, the atomization energy E of a molecule may be written as a sum of two contributions: a σ-bond energy and a π-bond energy.

$$E = E_{\sigma b} + E_{\pi b}\,. \tag{1}$$

$E_{\sigma b}$ and $E_{\pi b}$ being positive quantities.

Moreover, in this work, we suppose that each bond of the molecule contributes separately to the σ-bond energy:

$$E_{\sigma b} = \sum E_{\sigma n}$$

where n is the number of bonds in the molecule.

In order to take into account the effect of a possible delocalisation of π-electrons, we consider the π-bond energy as a whole, and write:

$$E_{\pi b} = -\left(E_{\pi} + E_N + \sum IP\right). \tag{2}$$

E_{π}, which is a negative quantity, is the total electronic energy of π-electrons. E_N is the electrostatic repulsion energy of the cores formed by the nuclei and the electrons which do not form a π-bond.

$\sum IP$ represents the sum, restricted to π-electrons only, of the ionization potentials of carbon atoms in their valence state. For a trigonal carbon C_{tr}, the ionization potential which corresponds to the process $C_{(trtrtr\pi)} \rightarrow C^{+}_{(trtrtr)}$ is equal to 0.4101 a.u. [15]. For a digonal carbon C_{di}, it corresponds to the process $C_{(didi\pi\pi)} \rightarrow C^{++}_{(didi)}$ and it is equal to 1.288 a.u. [15].

1. Evaluation of $E_{\sigma b}$

The energy of each σ-bond is considered to depend on its nature, on its length, and on the hybridization state of the linked atoms.

It is known that the energy of formation of paraffins cannot be expressed accurately as a sum of bond energies. The discrepancies are generally ascribed to some non-bonded interactions. Following DEWAR and SCHMEISING [7], we have taken these effects into account by considering different values for the energy of the bond between a hydrogen atom and a tetragonal carbon atom according to the primary, secondary or tertiary character of the carbon atom. The available data show that it is not necessary to modify the other C–H and C–C bonds according to the number and the nature of the adjacent bonds.

In the case of molecules which contain an isolated multiple bond, we consider, as a constant, the contribution of this bond to the energy, i.e. the sum of its π- and σ-bond energies (localized bond).

We have deduced a series of values of C–C and C–H bond energies, depending on the hybridization state of the carbon atoms, the length of the bonds and their relative position, by using the energy of formation [1] at 0 °K of the following hydrocarbons: ethane, n-hexane, isobutane, neopentane, ethylene, 1-hexene, acetylene and 1-hexyne, and by supposing that, in the non conjugated compound the variation ΔE in bond energy is proportional to the variation ΔR in the length of the same bond, when the variations ΔE and ΔR are small. The hypothesis of the proportionality between ΔE and ΔR has been successively applied to the bonds C_{te}–H, C_{tr}–H and C_{te}–C_{te}, C_{tr}–C_{te} and to the bonds C_{te}–H, C_{di}–H and C_{te}–C_{te}, C_{di}–C_{te}. For the C–H bond lengths, we have considered the spectroscopical values given by STOICHEFF [31] in the case of ethane, ethylene and acetylene, and for the C–C bond lengths, we have adopted the values proposed by LIDE [19]. The values of bond energies we have finally obtained by this method are given in Tab. 1.

Table 1. *Bond energies deduced from experimental data* (0 °K)

Bond	R(Å)	E(kcal m^{-1})	Bond	R(Å)	E(kcal m^{-1})
C_{te}–$H_{primary}$	1.102	97.12	C_{te}–C_{te}	1.526	84.33
C_{te}–$H_{secondary}$		96.45	C_{te}–C_{tr}	1.501	88.00
C_{te}–$H_{tertiary}$		95.99	C_{te}–C_{di}	1.459	92.91
C_{tr}–H	1.086	99.47	C_{tr}=C_{tr}	1.335	134.86
C_{di}–H	1.061	102.37	C_{di}≡C_{di}	1.206	184.95

These bond energies are obtained from the energy of formation at 0 °K of some hydrocarbons and by supposing that, in non-conjugated compounds the variation ΔE in bond energies is proportional to the variation ΔR in the length of the same bonds, when the variations ΔE and ΔR are very small.

According to BAK and HANSEN-NYGAARD [2], the variations observed in the length of C–C bonds are due not only to the change in the hybridization state of bound carbons, but also to the delocalization of electrons along the different bonds. From the experimental value of the distance C_{te}–C_{te} in diamond and by using the following relation [4]:

$$r_C = k\,(1 + \tfrac{4}{3}\sqrt{3}\,\lambda + \tfrac{3}{2}\lambda^2)/(1 + \sqrt{3}\,\lambda + \lambda^2)$$

which gives the covalent radius for a carbon atom in a given state of hybridization, as a function of the mixing coefficient λ, the preceding authors propose a series of values for the length of a single bond between two carbons in a given hybridization state when the bonds are not perturbed by any electronic delocalization. We have adopted these values as equilibrium distances R_{eq} between two carbon atoms.

The bond energies $E(R)$ we have obtained so far, are relative to experimental C–C distances, which are measured in non-conjugated compounds and which are smaller than the equilibrium distances (Tab. 1). The values of the equilibrium bond energies E_{eq}, shown in Tab. 2, have been calculated from the experimental

Table 2. *Equilibrium bond energies* (0 °K)

Bond	R(Å)	a(Å^{-1})	E(kcal m^{-1})
C_{te}–C_{te}	1.5445	1.9587	84.45
C_{te}–C_{tr}	1.5309	1.9574	88.32
C_{tr}–C_{tr}	1.5174	1.9562	92.19
C_{te}–C_{di}	1.5055	2.0448	93.85
C_{di}–C_{di}	1.4666	2.1453	103.25
C_{tr}–C_{di}	1.4920	2.0475	97.72
C_{tr}=C_{tr}	1.335	2.2639	134.86
C_{di}≡C_{di}	1.206	2.4722	184.95

These bond energies concern bonds, whose length is equal to the equilibrium distances proposed by Bak and Hansen-Nygaard. They are obtained from the data of Tab. 1 by using a Morse function to take the variation in bonds length into account.

values $E(R)$ and by taking the variation of bond lengths into account by using a Morse function.

Values of E_{eq} (C_{tr}–C_{tr}), E_{eq} (C_{di}–C_{di}) and E_{eq} (C_{di}–C_{tr}) have been obtained from the following approximate relations:

$$E_{eq}\,(C_{tr}–C_{te}) = \tfrac{1}{2}\,\{E_{eq}\,(C_{te}–C_{te}) + E_{eq}\,(C_{tr}–C_{tr})\}$$
$$E_{eq}\,(C_{di}–C_{te}) = \tfrac{1}{2}\,\{E_{eq}\,(C_{te}–C_{te}) + E_{eq}\,(C_{di}–C_{di})\}$$
$$E_{eq}\,(C_{tr}–C_{di}) = \tfrac{1}{2}\,\{E_{eq}\,(C_{tr}–C_{tr}) + E_{eq}\,(C_{di}–C_{di})\}\,.$$

The value of the constant a of the Morse equation depends on E_{eq}; in each case, it is determined by an iterative process. We have adopted six different values for the force constant relative to the bonds, according to the hybridization state of carbons of single bonds C–C [*30*].

We are now able to calculate the σ-bond energy $E(R)$ as a function of R, using the same Morse relation. Values of single C–C bond energies, for some particular values of R, are given in Tab. 3.

With the values of Tab. 1, it is possible to reproduce satisfactorily the atomization energy at 0 °K of all non conjugated hydrocarbons. In Tab. 4, we can see that the largest difference between the observed and the calculated values is 1.3 kcal m^{-1}, and that the mean deviation is 0.2 kcal m^{-1}. One sees, moreover that the order of thermodynamical stability of different isomers is satisfactorily reproduced.

Table 3. *Bond energies* (0 °K)

Bond	R(Å)	E(kcal m^{-1})	Bond	R(Å)	E(kcal m^{-1})
C_{tr}–C_{tr}	1.476	91.53	C_{di}–C_{di}	1.378	98.73
	1.460	90.98		1.206	45.32
	1.397	85.69	C_{di}–C_{tr}	1.440	96.49
	1.390	84.81		1.309	77.53
	1.350	78.35			
	1.335	75.24			

These bond energies are calculated from the data of Tab. 2, by using a Morse function to take the variation in length into account.

Table 4. *Atomization energies of non-conjugated hydrocarbons* (0 °K, kcal m^{-1})

Compounds	$E_{obs.}$	$E_{calc.}$	Compounds	$E_{obs.}$	$E_{calc.}$
ethane	667.0	(667.0)	trans-2-pentene	1369.4	1369.7
propane	943.6	944.2	2-methyl-1-butene	1370.5	1369.8
n-butane	1221.4	1221.5	3-methyl-1-butene	1368.8	1368.6
iso-butane	1223.1	(1223.1)	2-methyl-2-butene	1371.8	1372.4
n-pentane	1498.6	1498.7	1-hexene	1644.3	(1644.3)
iso-pentane	1500.2	1500.3	trans-2-hexene	1646.9	1646.9
neopentane	1502.7	(1502.8)	trans-3-hexene	1646.7	1646.9
n-hexane	1775.9	(1775.9)	2-methyl-1-pentene	1647.8	1647.0
2-methyl-pentane	1777.1	1777.5	3-methyl-1-pentene	1645.3	1645.9
3-methyl-pentane	1777.0	1777.5	1-4-pentadiene	1235.3	1235.4
2-2-dimethyl-butane	1779.7	1780.0	acetylene	389.7	(389.7)
2-3-dimethyl-butane	1777.8	1779.1	propyne	671.6	671.6
ethylene	532.7	(532.7)	1-butyne	948.5	948.8
propene	812.4	812.6	2-butyne	952.2	953.5
1-butene	1089.6	1089.9	1-pentyne	1226.0	1226.0
trans-2-butene	1092.3	1092.5	2-pentyne	1229.4	1230.7
iso-butene	1093.5	1092.5	3-methyl-1-butyne	1227.5	1227.6
1-pentene	1367.0	1367.1	1-hexyne	1503.3	(1503.3)

These atomization energies are obtained from the data reported in Tab. 1.

2. *Evaluation of* E_π

The axes of the $2p\,\pi$ atomic orbitals of the different carbon atoms linked by a double or a triple bond are supposed to be either parallel or perpendicular. Let θ be the value of the angle made by these axes. The atomic orbitals are called $\chi_p, \chi_q \ldots$ when θ is equal to 0° and $\chi_{p'}, \chi_{q'} \ldots$ when θ is equal to 90°.

χ_p and $\chi_{p'}$ are thus two $2p\,\pi$ atomic orbitals centred on the same atom p.

In the calculation of E_π, we have adopted the semi-empirical method proposed by PARISER and PARR [*23*] and by POPLE [*24*]. It is first of all necessary to extend this method to the case of acetylenic derivatives. This was already attempted by SERRE in her study of U.V. transitions in various derivatives of acetylene [*26*], vinylacetylenes and cumulenes [*27*]. Moreover, as we shall see later on, in order to arrive at a satisfactory calculation of the formation energies, we had to reconsider the semi-empirical evaluation of the different integrals which occur in the application of the method.

The π-electrons total energy is given by the usual formula:

$$E_\pi = \tfrac{1}{2} \sum_{p,q} P_{pq}\,(H^c_{pq} + H^{\text{SCF}}_{pq})\,. \tag{3}$$

To calculate the matrix elements H^{SCF}_{pq}, we use the formulas:

$$H^{\text{SCF}}_{pp} = \alpha_p = \alpha^c_p + \tfrac{1}{2} P_{pp}\,(pp, pp) + \sum_{q \neq p} P_{qq}\,(pp, qq) + \sum_{q' \neq p'} P_{q'q'}\,(pp, q'q') + $$
$$+ P_{p'p'}\,(pp, p'p') - \tfrac{1}{2} P_{p'p'}\,(pp', pp')$$

and

$$H^{\text{SCF}}_{pq} = \beta_{pq} = \beta^c_{pq} - \tfrac{1}{2} P_{pq}\,(pp, qq) - \tfrac{1}{2} P_{p'q'}\,(pp', qq')\,.$$

When a hydrocarbon contains at the same time double and triple bonds, the contribution of π-electrons to the energy takes the form:

$$E_\pi = \sum_p P_{pp}\,\alpha_p^c + 2 \sum_{p,q>p} P_{pq}\,\beta_{pq}^c + \tfrac{1}{4} \sum_p P_{pp}^2\,(pp, pp) + \tfrac{1}{2} \sum_{p,p'} P_{pp}\,P_{p'p'}$$
$$(pp, p'p') + \sum_{p,q>p} \{P_{pp}\,P_{qq} - \tfrac{1}{2} P_{pq}^2\}\,(pp, qq) + \sum_{p,q'>p'} P_{pp}\,P_{q'q'}$$
$$(pp, q'q') - \tfrac{1}{2} \sum_{p,q>p} P_{pq}\,P_{p'q'}\,(pp', qq') - \tfrac{1}{4} \sum_{p,p'} P_{pp}\,P_{p'p'}\,(pp', pp') \qquad (4)$$

where p represents successively the electrons $p, q, \ldots p', q', \ldots$

In the case of acetylene, for example, where the four π-electrons are designated by 1, 2, 1′, 2′, we have:

$$E_\pi = P_{11}\,\alpha_1^c + P_{22}\,\alpha_2^c + P_{1'1'}\,\alpha_{1'}^c + P_{2'2'}\,\alpha_{2'}^c + 2\,P_{12}\,\beta_{12}^c + 2\,P_{1'2'}\,\beta_{1'2'}^c +$$
$$+ \tfrac{1}{4} P_{11}^2\,(11, 11) + \tfrac{1}{4} P_{22}^2\,(22, 22) + \tfrac{1}{4} P_{1'1'}^2\,(1'1', 1'1') + \tfrac{1}{4} P_{2'2'}^2$$
$$(2'2', 2'2') + \tfrac{1}{2} P_{11}\,P_{1'1'}\,(11, 1'1') + \tfrac{1}{2} P_{1'1'}\,P_{11}\,(1'1', 11) + \tfrac{1}{2} P_{22}\,P_{2'2'}$$
$$(22, 2'2') + \tfrac{1}{2} P_{2'2'}\,P_{22}\,(2'2', 22) + \{P_{11}\,P_{22} - \tfrac{1}{2} P_{12}^2\}\,(11, 22) +$$
$$+ \{P_{1'1'}\,P_{2'2'} - \tfrac{1}{2} P_{1'2'}^2\}\,(1'1', 2'2') + P_{11}\,P_{2'2'}\,(11, 2'2') + P_{1'1'}\,P_{22}\,(1'1', 22) -$$
$$- \tfrac{1}{2} P_{12}\,P_{1'2'}\,(11', 22') - \tfrac{1}{2} P_{1'2'}\,P_{12}\,(1'1, 2'2) - \tfrac{1}{4} P_{11}\,P_{1'1'}\,(11', 11') -$$
$$- \tfrac{1}{4} P_{1'1'}\,P_{11}\,(1'1, 1'1) - \tfrac{1}{4} P_{22}\,P_{2'2'}\,(22', 22') - \tfrac{1}{4} P_{2'2'}\,P_{22}\,(2'2, 2'2)\,.$$

The latter equation can be written:

$$E_\pi = 4\,P_{11}\,\alpha_1^c + 4\,P_{12}\,\beta_{12}^c + P_{11}^2\,(11, 11) + 2\,P_{11}\,P_{1'1'}\,(11, 1'1') +$$
$$+ 2\,\{P_{11}\,P_{22} - \tfrac{1}{2} P_{12}^2\}\,(11, 22) + 2\,P_{11} P_{2'2'}\,(11, 2'2') - P_{1'2'}\,P_{12}\,(11', 22') -$$
$$- P_{11}\,P_{1'1'}\,(11', 11')\,.$$

In the formula (4), we find the usual terms:

$$P_{pq} = 2 \sum_i C_{ip}\,C_{iq}$$

where C_{ip} and C_{iq} are the coefficients of atomic orbitals χ_p, χ_q in the expression of the molecular orbital φ_i

$$\varphi_i = \sum_p C_{ip}\,\chi_p$$

and the usual integrals:

$$H_{pp}^c = \alpha_p^c = \int \chi_p^*\,(1)\,H^c\,(1)\,\chi_p\,(1)\,d\tau$$
$$H_{pq}^c = \beta_{pq}^c = \int \chi_p^*\,(1)\,H^c\,(1)\,\chi_q\,(1)\,d\tau$$
$$(pp, qq) = \int \chi_p^*(1)\,\chi_p\,(1)\,(1/R_{pq})\,\chi_q^*\,(2)\,\chi_q\,(2)\,d\tau \qquad \text{in a.u.}$$

where $H^c\,(1)$ is the one-electron core operator, and $(1/R_{pq})$ is the bielectronic operator associated with the repulsion between electrons.

a) Evaluation of P_{pq}

These terms are evaluated from the coefficients of atomic orbitals in the expression of molecular orbitals, calculated by the SCF LCAO method.

In the case of naphtalene and styrene, we have simply taken the molecular orbitals given by Coulson and Streitwieser [5]. In the case of naphtalene, the use of the SCF molecular orbitals reported by Hoyland and Goodman [14] was found to lead to a very small improvement only; the atomization energy of naphtalene is equal to 2074.0 kcal m^{-1} in the first calculation, and to 2075.8 kcal m^{-1}, in the second one.

b) Evaluation of core integrals α_p^c

Pariser and Parr [23] give for α_p^c the following expression:

$$\alpha_p^c = W_p - \sum_{q \neq p,p'} [(pp, qq) + (q:pp)] - \sum_r (r:pp) \tag{5}$$

where r is an atom giving no π-electrons.

$(q:pp)$ and $(r:pp)$ are penetration integrals .

W_p is the energy of the electron which is described by the π_x orbital in the carbon atom. In the case of an ethylenic carbon, the atom is formed by a core C^+ and by this electron in the π_x orbital. In the case of an acetylenic carbon, it is formed by a core C^{++} and by two electrons, one in the π_x orbital and the second in the π_y orbital. For the electron of a trigonal carbon, W_p is equal to the opposite of the ionization potential of the carbon atom in its valence state *trtrtrπ*, i.e. −0.410141 a.u. For an electron of a digonal carbon, we have adopted the value −0.791249 a.u. This value has been obtained from the second ionization of carbon in its valence state *didiππ*, modified as suggested by Leroy [18] in order to take the orbital effective nuclear charge into account ($Z = 3.25$).

If penetration integrals are neglected, the preceding expression becomes:

$$\alpha_p^c = W_p - \sum_{q \neq p,p'} (pp, qq) \,. \tag{6}$$

In the present method, penetration integrals are taken into account in spite of the fact that the simplified expression (6) is used for α_p^c. One sees easily that the ionization potential of a given carbon occurs twice, in expression (2), but with different signs: once in the term $\sum IP$, and once in the term $\sum_p P_{pp}\, \alpha_p^c$ (where P_{pp} is practically equal to unity). In the case of ethylene, for instance, we use in the first term the ionization potential of C_{tr} instead of the ionization potential of the group formed by a trigonal carbon surrounded by two hydrogen atoms and a carbon atom. This amounts to neglecting the penetration integrals due to the interaction between the π-electron and the neighbouring atoms. In the second term, we use the ionization potential of C_{tr}, neglecting, in the same way, the penetration integrals considered in eq. (5). Finally, we have, in the expression of $E_{\pi b}$, a cancellation of penetration integrals which justifies the described approximation.

c) Evaluation of Core Integrals β_{pq}^c

A critical examination of the different methods of evaluating β_{pq}^c which have been proposed so far, leads to the conclusion that there is only one suitable method for the calculation of atomization energies. This method has been proposed by Dewar and Schmeising [8] and by Oleari and Di Sipio [21]. These authors do not calculate the integrals β_{pq}^{c} from the values of spectroscopic transitions, but from the total bonding energy of a molecule. From the experimental values of the atomization energy of ethylene and acetylene, one obtains a relation between β^c and the distance R between either two trigonal carbons or two digonal carbons. This process will now be briefly described in the case of $\beta^{C}{}_{(C_{tr},C_{tr})}$.

The energy of an isolated double bond of length R may be represented by the Morse equation:

$$E(R) = E_{eq\ (C_{tr}=C_{tr})}\,[2\exp\{-a_1(R-R_{eq})\} - \exp\{-2a_1(R-R_{eq})\}]\,. \quad (7)$$

$E_{eq\ (C_{tr}=C_{tr})}$ is the value of the double bond energy between two trigonal carbons at the experimental distance $R_{eq} = 1.335$ Å; it is equal to 134.86 kcal m^{-1} (Tab. 2).

The same energy $E(R)$ can also be expressed by the following relation, where π- and σ-electrons contributions are separated:

$$E(R) = \{E_{eq\ (C_{tr}-C_{tr})} - E_{\mathrm{comp}}\} - \{E_{\pi} + E_N + \sum IP\}\,. \quad (8)$$

In this relation, $E_{eq\ (C_{tr}-C_{tr})}$ is the value of the energy of a σ-bond between two trigonal carbons at the equilibrium distance (92.19 kcal m^{-1}).

E_{comp} is the energy which is necessary to contract the single bond from the equilibrium value 1.5174 Å to the value R.

$$E_{\mathrm{comp}} = E_{eq}\,[1 + \exp\{-2\,a_2(R-R_{eq})\} - 2\exp\{-2\,a_2(R-R_{eq})\}]\,.$$

In the relation (8), we have:

$$E_{\pi} + E_N + \sum IP = 2\,\beta^c + \tfrac{1}{2}(11, 11) - \tfrac{1}{2}(11, 22)\,.$$

E_N being considered equal to (11, 22) as explained later on.

Equating expressions (7) and (8), one finally obtains:

$$\begin{aligned} \beta^c{}_{(C_{tr},C_{tr})} = & -0.013644\,R^2 + 0.002426\,R^3 + \\ & + 0.073434\,[2\exp\{-1.9562\,(R-1.5174)\} - \\ & \qquad - \exp\{-2\times 1.9562\,(R-1.5174)\}] - \\ & - 0.107422\,[2\exp\{-2.2639\,(R-1.335)\} - \\ & \qquad - \exp\{-2\times 2.2639\,(R-1.335)\}] \quad \text{in a.u. } (R \text{ in Å}) \end{aligned} \quad (9)$$

by the same process, applied this time to acetylene, one gets:

$$\begin{aligned} \beta^c{}_{(C_{di},C_{di})} = & -0.017641 - 0.015224\,R^2 + 0.002747\,R^3 + \\ & + 0.041122\,[2\exp\{-2.1453\,(R-1.4666)\} \\ & \qquad - \exp\{-2\times 2.1453\,(R-1.4666)\}] - \\ & - 0.073661\,[2\exp\{-2.4722\,(R-1.206)\} \\ & \qquad - \exp\{-2\times 2.4722\,(R-1.206)\}] \quad \text{in a.u. } (R \text{ in Å})\,. \end{aligned} \quad (10)$$

In order to obtain $\beta^c{}_{(C_{tr},C_{di})}$ as a function of R, we have supposed that:

$$\beta^c{}_{(C_{tr},C_{di})} = \tfrac{1}{2}\{\beta^c{}_{(C_{tr},C_{tr})} + \beta^c{}_{(C_{di},C_{di})}\}\,. \quad (11)$$

Tab. 5 gives the values we have adopted for β^c in our subsequent calculations.

Let us now remember that we consider $E_{\sigma b}$ as the sum of σ-bond energy terms, and that these terms do not include a contribution representing the zero-point energy. In the calculation of the compression energies, we continue to use, in the Morse equation, the same values of σ-bond energies and, therefore, neglect the

Table 5. *Core integrals* β^c

Bond	R(Å)	$-\beta^c$(a.u.)	$-\beta^c$(eV)	Bond	R(Å)	$-\beta^c$(a.u.)	$-\beta^c$(eV)
C_{tr}–C_{tr}	1.273	0.076249	2.07	C_{di}–C_{di}	1.206	0.090575	2.46
	1.309	0.070133	1.91		1.273	0.078369	2.13
	1.335	0.066033	1.80		1.309	0.073037	1.99
	1.35	0.063788	1.74		1.378	0.064866	1.77
	1.390	0.058245	1.58		1.440	0.059475	1.62
	1.397	0.057340	1.56	C_{di}–C_{tr}	1.273	0.077309	2.10
	1.440	0.052191	1.42		1.309	0.071585	1.95
	1.46	0.050033	1.36		1.440	0.055833	1.52
	1.476	0.048411	1.32				

The values of β^c are calculated from the three relations $\beta^c(R)$ (9) (10) (11) described in the paragraph 2-c.

zero point energy. By this process, the maximal error is about 2.5% on a correction term. (According to CHUNG and DEWAR [3], in benzene, the contribution to the zero-point energy of a C–C σ-bond is about 2 kcal m^{-1} while, for the σ-bond energy itself, we use the value 86 kcal m^{-1}.)

Actually, this error is still much smaller, because the values of β^c have been obtained by a calculation of the atomization energy of ethylene and acetylene, where the preceding approximation has been made.

The use of the same values of β^c, in the calculation of the atomization energy of other hydrocarbons, must decrease the error to a large extent.

d) Evaluation of the Electronic Repulsion Integrals (pp, qq)

The one-center integral (pp, pp) is calculated by PAOLONI's formula [22]; it has the same value of 0.393603 a.u. for trigonal and digonal carbons. In order to get the value of the integral $(pp, p'p')$, we have supposed that the ratio between the integrals (pp, pp) and $(pp, p'p')$ was equal to its theoretical value, evaluated from ROOTHAAN's tables [25]; the adopted value is 0.350973 a.u.

The integral (pp', pp'), calculated by the relation:

$$(pp', pp') = \tfrac{1}{2}\{(pp, pp) - (pp, p'p')\} \qquad \text{is equal to } 0.021315 \text{ a.u.}$$

When the internuclear distances R are greater than 2.8 Å, the two-center integrals are calculated by using the uniformly charged sphere approximation [23]. When R is smaller than 2.8 Å, they are obtained from a polynomial, chosen so that the curve representing the variation of the integral (pp, qq) as a function of R, has a slope equal to zero at the origin. The following expressions were used:

$$(pp, qq) = 0.393603 - 0.054575\, R^2 + 0.009702\, R^3 \qquad \text{a.u. } (R \text{ in Å})$$

and

$$(pp, q'q') = 0.350972 - 0.041933\, R^2 + 0.007130\, R^3 \qquad \text{a.u. } (R \text{ in Å})$$

The integrals (pp', qq') are calculated by the relation:

$$(pp', qq') = \tfrac{1}{2}\{(pp, qq) - (pp, q'q')\}\,.$$

3. *Evaluation of E_N*

In order to calculate the nuclear energy E_N, different functions were tried (see Appendix). We have, finally, adopted the relation:

$$E_N = \sum_{p>q} (pp, qq) \tag{12}$$

where p and q are $2p\,\pi$ atomic orbitals situated on different carbons.

Results and Discussion

Substituting (6) and (12) in (1), one finally obtains the general formula:

$$\begin{aligned} E = E_{\sigma b} - (E_\pi + E_N + \sum IP) = E_{\sigma b} - [\sum IP + \sum_p P_{pp}\, W_p + 2 \sum_{p,q>p} P_{pq}\, \beta^c_{pq} + \\ + \tfrac{1}{4} \sum_p P^2_{pp}\, (pp, pp) + \tfrac{1}{2} \sum_{p,p'} P_{pp}\, P_{p'p'}\, (pp, p'p') + \sum_{p,q>p} \{P_{pp}\, P_{qq} - \tfrac{1}{2} P^2_{pq} + 1 - \\ - P_{pp} - P_{qq}\}\, (pp, qq) + \\ + \sum_{p,q'>p'} \{P_{pp}\, P_{q'q'} + 1 - P_{pp} - P_{q'q'}\}\, (pp, q'q') - \tfrac{1}{4} \sum_{p,p'} P_{pp}\, P_{p'p'}\, (pp', pp') - \\ - \tfrac{1}{2} \sum_{p,q>p} P_{pq}\, P_{p'q'}\, (pp', qq')] \end{aligned} \tag{13}$$

where p represents successively electrons $p, q, \ldots p', q', \ldots$

The atomization energy of some conjugated hydrocarbons has been calculated by this formula. The comparison between these calculated values and the available experimental data is made in Tab. 6.

The experimental information on the thermodynamical stability of conjugated acetylenic hydrocarbons is unfortunately very scarce. For that reason, is was only possible to test the validity of the approximations we have proposed, in a indirect manner, from a consideration of the experimental values of the heat of hydrogenation of some acetylenic derivatives. Moreover, since these experimental measurements are made at 298 °K and in solution, it is necessary to make several corrections before comparing them with our calculated values. Under these conditions, a very good agreement between the two sets of values cannot be expected.

The following method was used, in order to make the correction for the difference of temperature. We have calculated the difference between the heat of hydrogenation, at 0 °K and at 298 °K, of all unsaturated hydrocarbons for which

Table 6. *Atomization energies of conjugated hydrocarbons* (0 °K, kcal m^{-1})

Compounds	$E_{obs.}$	$E_{calc.}$	Compounds	$E_{obs.}$	$E_{calc.}$
1-3-butadiene	961.5	964.4	1-2-pentadiene	1225.6	1222.4
trans-1-3-pentadiene	1241.5	1244.3	vinylacetylene	—	824.6
benzene	1308.1	1309.5	butadiyne	—	691.1
toluene	1588.2	1589.3	divinylacetylene	—	1259.8
p-xylene	1868.2	1869.2	butadienylacetylene	—	1256.5
styrene	1735.8	1736.2	hexadiyne 1-3	—	1250.3
naphtalene	2076.0	2075.8	hexadiyne 2-4	—	1254.9
allene	670.0	665.3	hexadiyne 1-5	—	1230.6
1-2-butadiene	949.3	945.2	diallene	—	1229.6

Calculated values obtained from the general formula (13).

the necessary data were known. One finds that this difference is an additive property, which can be expressed as the sum of contributions of the different multiple bonds of the hydrocarbon, irrespective of their conjugation. One arrives at this conclusion by considering conjugated as well as non-conjugated hydrocarbons such as ethylene, acetylene, benzene, 1-2, 1-3, 1-4 pentadiene etc ...

The contribution of a double bond is 1.6 ± 0.2 kcal m^{-1}; that of a triple bond is 3.4 ± 0.3 kcal m^{-1}.

SKINNER et al. [*11*, *29*] have measured the heat of hydrogenation of hexadiyne 1-5 and of dodecadiyne 5-7. At 298 °K and in the liquid state, the authors propose a value of -139.4 ± 1.0 kcal m^{-1} for hexadiyne 1-5, while at 0 °K and in the gas state we calculate a value of -132.3 kcal m^{-1}. If the difference of temperature is taken into account, by applying a correction of 6.8 kcal m^{-1} (correction for two triple bonds) to the experimental value, one gets a value of -132.6 kcal m^{-1} which is comparable to our calculated value.

The experimental heat of hydrogenation of dodecadiyne 5-7 is equal, at 298 °K and in the liquid state, to -127.2 ± 0.7 kcal m^{-1}. With the preceding correction, we expect, at 0 °K, a heat of hydrogenation of about -120.4 kcal m^{-1} while the calculation gives a value of -108 kcal m^{-1}.

At 0 °K and in the gas state, we calculate, for pent-3-en-1-yne and for pent-1-en-3-yne, heats of hydrogenation of -84.7 and -82.7 kcal m^{-1} respectively. At 298 °K and in the liquid state, SKINNER et al. measure, for the same substances, or for comparable ones, heats of hydrogenation of -96.0 and -92.3 kcal m^{-1}. If we apply the appropriate correction of 5 kcal m^{-1} to the experimental values (correction for one double bond and one triple bond), we calculate at 0 °K, for pent-3-en-1-yne, a heat of hydrogenation of 84.7 instead of 91 kcal m^{-1} and, for pent-1-en-3-yne, 82.7 instead of 87.3 kcal m^{-1}.

The available experimental informations are indirect and too scarce to allow any meaningful comparison. It seems, however, possible that our calculated atomization energies are somewhat too large, especially in the case of conjugated acetylenic derivatives. An accurate knowledge of the heat of formation of, e.g., diacetylene and vinylacetylene, would provide a starting point for an improvement of the treatment we propose, by only modifying minor details. A slight decrease of the value of the integral (pp, pp) and some modification of the value of the term W_p in the case of an acetylenic carbon might lead to a better agreement.

In conclusion, we feel that the method just described can be expected to give reasonably reliable values of the atomization energy of all hydrocarbons, in any hybridization state of the carbon atoms.

In another connection, it is important to emphasize that this method is limited to the calculation of atomization energies only. We have already stressed the fact that the expression of $\beta^c(R)$ has been obtained by equating the experimental value of the energy of ethylene or acetylene to an approximate expression. The approximations involved in the model will, therefore, directly influence the value of β^c. Since, however, the same relation is then used in the calculation of the energy of other hydrocarbons, the errors introduced by these approximations will, to a large extent, cancel out. This will also be true for the error due to inaccuracy of the separation of atomization energy into a π- and a σ-component.

But, by the same token, one also expects that particular values of β^c are only appropriate for the calculation of one specified property. For a given bond, different values of β^c must be considered according to the property one calculates. It seems, for example, that it is not possible to get values of β^c which are satisfactory for the simultaneous calculation of the atomization energy and the U.V. spectrum. The values appropriate for the atomization energies are much too small when U.V. spectra are considered. Conversely, the standard values of β^c, which have been derived from spectroscopic studies will never be satisfactory for the calculation of ground state energies. Analogous remarks may be made in the case of ionization energies calculations. This situation is hardly surprising, if one remembers that the original definition of β^c is entirely empirical [*23*].

Atomization Energy of Radicals

In the case of radicals deriving from saturated hydrocarbons by the removal of one hydrogen atom, the π-system is formed by only one electron localized on the carbon losing the hydrogen atom. In these conditions, eq. (2) becomes:

$$E_\pi + E_N + \sum PI = - PI + PI = 0 \, .$$

There is no π-contribution to the atomization energy, which therefore reduces to the sum of σ-bond energies.

The atomization energy at 0 °K of some C_nH_m radicals was calculated from the values of the σ-bond energies which were used previously. A temperature correction was then applied, by considering the difference between the experimental atomization energy at 0 °K and at 298 °K in the case of the saturated and ethylenic hydrocarbons C_nH_{m+1} and C_nH_{m-1} with a similar structure. In the case of the t-C_4H_9, for example, a correction term of 15.4 kcal m^{-1} was added to the calculated value at 0 °K. This correction represents the mean value of the difference between the experimental atomization energies measured at 298 °K and at 0 °K for isobutane (16.8 kcal m^{-1}) and for isobutene (14.0 kcal m^{-1}).

The values of the atomization energy calculated at 0 °K, estimated at 298 °K and measured at the same temperatures are given in Tab. 7. The difference between the calculated and the experimental values, which is more important for the small radicals, depends especially on the number of C_{tr}–H bonds present in the system. The use of a value of the C_{tr}–H bond energy slightly smaller than the value which was considered in the case of hydrocarbons would lead to a better agreement.

Table 7. *Atomization energy of radicals* (kcal m^{-1})

Radicals	$E_{calculated}$ (0 °K)	$E_{measured}$ (0 °K)	$E_{estimated}$ (298 °K)	$E_{measured}$ (298 °K)
CH_3	298	292 [*1*]		296 [*1*]
C_2H_5	578		586	578 [*10*], 579 [*13*], 580 [*10*]
n–C_3H_7	855		867	858 [*10*], 861 [*9*], 862 [*10*]
s–C_3H_7	858		870	861 [*10*], 868 [*10*]
n–C_4H_9	1133		1148	1137 [*10*], 1144 [*10*]
t–C_4H_9	1138		1153	1150 [*10*], 1153 [*10*]
C_2H_3	420		425	417 [*10*], 432 [*16*], 435 [*12*]
C_3H_5	731		741	743.5 ± 6 [*20*]

In the case of open shell systems, the relation (13) is no longer applicable for the calculation of atomization energy.

The atomization energy of the radicals C_2H_3 and C_3H_5 (allyl radical) was obtained by calculating E_π from the definition of the total electronic energy of π-electrons:

$$E_\pi = \int \Psi H \Psi d\tau$$

where Ψ is the wave function which represents the ground state of the considered system and which has the usual form of a normalized determinant, built on SCF orthonormalized molecular orbitals. These latter orbitals were determined by using the method proposed by LEFEBVRE [*17*]. The different integrals and matrix elements, which are necessary in the calculation of E, were obtained by the methods already described.

At 0 °K, the calculated atomization energy of the radical C_2H_3 is 420 kcal m^{-1}. From this value, it is possible to deduce a reasonably reliable value of the atomization energy at 298 °K, by considering the difference between the atomization energy measured respectively at 0 °K and at 298 °K, for the molecules C_2H_4 (6.6 kcal m^{-1}) and C_2H_2 (3.7 kcal m^{-1}). Taking the average of these values in the case of C_2H_3, one gets for this radical an atomization energy, at 298 °K, of 425 kcal m^{-1}. The experimental measurements give the values: 417, 432 and 435 $\pm$ 3 kcal m^{-1}.

At 0 °K, the calculated atomization energy of the radical C_3H_5 is 731 kcal m^{-1}. Its atomization energy at 298 °K, estimated from the atomization energies of the molecules C_3H_6 and C_3H_4, is equal to 741 kcal m^{-1}. At the same temperature, the experimental value is 743.5 $\pm$ 6 kcal m^{-1}.

The results of these calculations seem to show that the energy of formation of radicals can be calculated with the same accuracy as the energy of formation of hydrocarbons.

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Appendix

This appendix is a summary of the methods which were tried in the evaluation of the different terms and integrals. We have finally adopted the method which gives the best result in the calculation of the atomization energy of benzene.

Evaluation of $E_{\sigma b}$. We have deduced two series of values for the energy of C–C and C–H bonds. The first series, which is designated by $E_\sigma(a)$, was obtained by taking only one value for the energy of $(C_{te}\text{–}H)_{\text{primary}}$, $(C_{tr}\text{–}H)$ and $(C_{di}\text{–}H)$ bonds. The second method is the one described in the text; the set of values it gives is designated by E_σ (b). In both methods, the effects of non-bonded interactions have been taken into account by considering different values for the energy of the bond between a hydrogen atom and a tetragonal carbon atom according to the primary, secondary or tertiary character of the carbon atom. In the calculation of the atomization energy of non-conjugated hydrocarbons, the two sets give equally good results, but they give different results in the case of conjugated derivatives.

When the series E_σ (b) is used instead of the series E_σ (a), the contribution $E_{\sigma b}$ increases and the contribution $E_{\pi b}$ decreases. In the case of benzene, the increase of $E_{\sigma b}$ is 40.5 kcal m^{-1} while the decrease of $E_{\pi b}$ is 54.6 kcal m^{-1}. The difference between the two values of the atomization energy of benzene is finally -14.1 kcal m^{-1}.

Evaluation of E_N. In the calculation of nuclear energies, we have tried two different relations: $E_N = \sum_{p \neq q} (pp, qq)$ which is designated by E_N (1) and $E_N = \sum_{p \neq q} R_{pq}^{-1}$ which is designated by E_N (2). The two approximations give very different results. In the case of benzene, if the approximation E_N (2) is considered instead of the approximation E_N (1), the atomization energy is decreased by an amount of 128.4 or 183.5 kcal m^{-1} according to the method used in the calculation of the other integrals. In all cases, the use of the relation E_N (2) gives too small atomization energies.

Evaluation of (pp, pp). This integral has been calculated, either by PAOLONI's formula [approximation designated by (pp, pp) (1)], or by the relation: $(pp, pp) = I_p - A_p$ which is designated by (pp, pp) (2). If the relation E_N (1) is used, the two approximations give almost the same result. An increase of 0.37 eV in the integral (pp, pp) increases the atomization energy of benzene by an amount of 1 kcal m^{-1}. As we have already pointed out in the discussion, it is possible that a slightly smaller value of this integral would lead to a general improvement of the numerical results.

Evaluation of (pp, qq). When $R \leq 2.80$ Å, we have tried two different polynomials for calculating the two-center integrals:

$$(pp, qq) = (pp, pp) + aR + bR^2 \text{ which is designated by } (pp, qq)\ (1)$$

and

$$(pp, qq) = (pp, pp) + aR^2 + bR^3 \text{ which is designated by } (pp, qq)\ (2)\,.$$

By using the second polynomial, the value of integrals (pp, qq) for small internuclear distances is increased, and better results in the calculation of atomization energies are obtained.

The values, which are reported in Tab. 6, are calculated by using the approximations: E_σ (b); E_N (1); (pp, qq) (2); (pp, pp) (1).

In the case of benzene, Tab. 8 shows the values of β^c and of E which are obtained in different calculations.

Influence of the Molecular Geometry. In one case, the influence of the molecular geometry on the calculated value of the atomization energy was also studied.

In the case of trans-butadiene, two different nuclear configurations were considered successively:

(a) $R_{12} = 1.335$ Å; $R_{23} = 1.476$ Å; $\sphericalangle = 120°$.
(b) $R_{12} = 1.350$ Å; $R_{23} = 1.460$ Å; $\sphericalangle = 124°$.

The following results are obtained:

(a) $E_{\sigma b} = 838.8$ kcal m^{-1}; $E_{\pi b} = 125.6$ kcal m^{-1}; $E = 964.4$ kcal m^{-1}.
(b) $E_{\sigma b} = 844.8$ kcal m^{-1}; $E_{\pi b} = 119.7$ kcal m^{-1}; $E = 964.5$ kcal m^{-1}.

Table 8. *Results of different calculations of the atomization energy of benzene*

Approximations	$-\beta^c$ (1.397 Å) (eV)	$E_{\text{benz.}}$ (kcal m^{-1})
E_σ (b); E_N (1); (pp, qq) (1); (pp, pp) (1)	1.82	1326.9
E_σ (b); E_N (1); (pp, qq) (2); (pp, pp) (1)	1.56	1309.7
E_σ (b); E_N (2); (pp, qq) (1); (pp, pp) (1)	3.25	1143.4
E_σ (b); E_N (2); (pp, qq) (2); (pp, pp) (1)	2.44	1181.3
E_σ (a); E_N (1); (pp, qq) (1); (pp, pp) (1)	2.12	1341.0
E_σ (a); E_N (1); (pp, qq) (2); (pp, pp) (1)	1.85	1323.7
E_σ (a); E_N (2); (pp, qq) (1); (pp, pp) (1)	3.54	1157.4
E_σ (a); E_N (2); (pp, qq) (2); (pp, pp) (1)	2.74	1195.3
E_σ (a); E_N (2); (pp, qq) (2); (pp, pp) (2)	2.67	1213.3
E_σ (b); E_N (1); (pp, qq) (2); (pp, pp) (2)	1.60	1310.7
Observed value for $E_{\text{benz.}}$		1308.1

The atomization energy is practically not modified, but the variation of its σ-component and the variation of its π-component are both equal to 6 kcal m^{-1} but with opposite signs.

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