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Charge Distributions and Chemical Effects. 23. The Chemical Bond, a Theory of Electron Density

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Abstract: The energy of atomization, ΔE_a^*, of a hypothetical vibrationless molecule is conveniently partitioned into bonded and nonbonded contributions. The portion of ΔE_a^* associated with the bond formed by atoms i and j (i.e., the "bond energy", ϵ_{ij}) can be deduced from the derivatives of ϵ_{ij} with respect to the nuclear charges of i and j. Bond energies derived for one molecule are not transferable to other molecules because, as a rule, the simple transfer of selected ϵ_{ij}'s would not satisfy the requirement for molecular electroneutrality. The appropriate charge renormalization accompanying the use of selected reference bond energies ϵ^0_{ij} leads to a description of the "bonded part" of ΔE_a^*, $\Delta E_a^{*\text{bonds}} = \sum\epsilon^0_{ij} + \sum_i\sum_j a_{ij}\Delta q_i$, featuring the effects due to changes in net atomic charges (Δq_i) with respect to the charges of the atoms forming the reference bonds. Theoretical expressions are given for the a_{ij} coefficients. Applications to saturated hydrocarbons indicate that the charge-dependent $\sum_i\sum_j a_{ij}\Delta q_i$ part is by far the leading term accounting for the energetic differences between isomers or conformers and that nonbonded coulomb interactions play an almost negligible role in that respect. The structural effects in linear and branched paraffins and in compounds containing chair or boat cyclohexane rings are deduced from the theoretical a_{ij}'s, indicating that 1 me ($=10^{-3}$ e) of electronic charge added to hydrogen stabilizes a CH bond by 0.632 kcal/mol, whereas 1 me added to carbon has a stabilizing effect of 0.247 on a CH bond and of 0.488 kcal/mol on a CC bond. The calculated molecular atomization energies agree with their experimental counterparts within 0.16 kcal/mol (average deviation).

Introduction

Several fundamental aspects of chemical binding are discussed in this paper, namely, the view that molecules can be regarded as assemblies of "chemical bonds" with energies of their own or, else, as collections of "atoms in the molecule" with energies differing from their free-state values. Various facets of energy partitioning are reviewed and expanded. The roles of electronic charge distributions and finally that of "steric effects" are analyzed in detail. The whole adds up to give a novel view of the important physical features governing molecular stabilities and casts a new light on relevant aspects facilitating the interpretation of organic chemistry. Numerical examples are worked out for saturated hydrocarbons in order to illustrate in a comprehensive way the detailed features of this unified picture of molecular energies. A qualitative description of the relevant results and implications in organic chemistry is offered in the Conclusions.

Theory

Relationships between Energy Components. A major part of the present theory is developed in the spirit of the Hellmann–Feynman theorem, which shows that a consideration of classical electrostatic interactions suffices to determine the energy of a molecular system without the need for *explicit* inclusion of quantum mechanical contributions.[1] The potential energy V is made up from nuclear–electronic (V_{ne}), electronic–electronic (V_{ee}), and, in molecules, also nuclear–nuclear (V_{nn}) contributions. It follows from the virial theorem that for atoms and molecules in their equilibrium geometry the total (kinetic + potential) energy E is

$$E = \tfrac{1}{2}(V_{ne} + V_{ee} + V_{nn}) \tag{1}$$

At the atomic level, a considerable simplification can be achieved with the use of the ratio K_k^{at} defined by eq 2, relating

$$E_k(\text{free atom}) = K_k^{at}V_{ne}(\text{free atom}) \tag{2}$$

the total energy E_k of a free atom k to its nuclear–electronic potential energy. The noteworthy point is that except for hydrogen, whose K_H^{at} value is obviously $^1/_2$ (eq 1), K_k^{at} always approaches the Thomas–Fermi limit $^3/_7$.[2-8] For carbon, namely, large basis set ab initio calculations indicate[8] $K_C^{at} = 1/2.3390$. Incidentally, eq 2 holds equally well if E_k and V_{ne} (free atom k) refer only to valence-shell electrons,[4,9-11] again with $K_k^{at} \simeq {}^3/_7$ for atoms other than hydrogen.

We now consider an atom k in a molecule. The corresponding nuclear–electronic interaction energy $V_{ne}(k,\text{mol})$ arises then from all electrons in the molecule, and the total potential energy involving nucleus Z_k is given in eq 3, where the sum over l runs over

$$V(k,\text{mol}) = V_{ne}(k,\text{mol}) + Z_k\sum_{l\neq k} Z_l/r_{lk} \tag{3}$$

all nuclei but k and r_{lk} is the distance from nucleus k to nucleus l. Defining now a quantity K_k^{mol} (similar to K_k^{at}) such that eq 4 represents the energy of atom k in a molecule, it follows that the sum $\sum E_k(\text{mol})$ over all the k's gives the molecular energy

$$E_k(\text{mol}) = K_k^{mol}\, V(k,\text{mol}) \tag{4}$$

defined in eq 5.

$$E_{mol} = \sum_k K_k^{mol}V(k,\text{mol}) \tag{5}$$

This, of course, is an expression for the molecular energy in terms of atomic-like contributions. Noting that

$$\sum_k K_k^{mol}V(k,\text{mol}) / \sum_k V(k,\text{mol}) = K_{Av}^{mol} \tag{6}$$

is just a weighted average value of the individual K_k^{mol}'s, it also follows that

$$E_{mol} = K_{Av}^{mol}\sum_k V(k,\text{mol}) = K_{Av}^{mol}(V_{ne} + 2V_{nn}) \tag{7}$$

Equations 5 and 7 are modifications of Politzer's formulas,[6,8,12] with the added clarification (eq 6) about the averaging of the K_k^{mol}'s. Equations 5 and 7 are amply substantiated.[6-9,12] The evidence[7] is that (except for hydrogen) the K_k^{mol} values are always close to $^3/_7$ and, consequently, that this holds also for K_{Av}^{mol}. This result includes the hydrocarbons because of the large weight of $V(\text{C,mol}) \simeq -89$ au compared to hydrogen, whose $V(\text{H,mol})$ is of the order of $\sim$−1 au. It is concluded that the original Politzer formula,[12] eq 8, represents a valid first approximation. Its use-

(1) R. P. Feynman, *Phys. Rev.*, **56**, 340 (1939); T. Berlin, *J. Chem. Phys.*, **19**, 208 (1951).
(2) S. Fraga, *Theor. Chim. Acta*, **2**, 406 (1964).
(3) P. Politzer and R. G. Parr, *J. Chem. Phys.*, **61**, 4258 (1974).
(4) P. Politzer and R. G. Parr, *J. Chem. Phys.*, **64**, 4634 (1976).
(5) R. G. Parr, R. A. Donnelly, M. Levy, and W. E. Palke, *J. Chem. Phys.*, **68**, 3801 (1978).
(6) P. Politzer, *J. Chem. Phys.*, **70**, 1067 (1979).
(7) T. Anno, *J. Chem. Phys.*, **72**, 782 (1980).
(8) S. Fliszár and M. T. Béraldin, *J. Chem. Phys.*, **72**, 1013 (1980).
(9) S. Fliszár and H. Henry, *J. Chem. Phys.*, **67**, 2345 (1977).
(10) S. Fliszár, *J. Chem. Phys.*, **69**, 237 (1978).
(11) S. Fliszár and D. Salahub, *J. Chem. Phys.*, **69**, 3321 (1978).
(12) P. Politzer, *J. Chem. Phys.*, **64**, 4239 (1976).

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$$E_{mol} \simeq {}^3\!/_7(V_{ne} + 2V_{nn}) \quad (8)$$

fulness depends, of course, on what is done with it. For our projected application, this approximation turns out to be sufficient. However, although K_{Av}^{mol} is in all cases near the $^3/_7$ limit, it is clear that its value is not strictly constant.[8] Equations 7 and 8 should therefore not be used abusively in problems where a postulated strict constancy of the $E_{mol}/(V_{ne} + 2V_{nn})$ ratio plays a crucial role.

Binding of an Atom in a Molecule. We can now proceed with the study of the energy difference (see eq 9) between a free and

$$\Delta E_k = E_k(\text{free atom}) - E_k(\text{mol}) \quad (9)$$

a bonded atom. ΔE_k is clearly a measure for the process of a free atom becoming part of a molecule and contains a portion of the molecular binding energy. The sum (eq 10) represents, accord-

$$\Delta E_a^* = \sum_k \Delta E_k \quad (10)$$

ingly, the total energy of atomization at 0 K of a molecule in its hypothetical vibrationless state. Introducing at this stage the concept of "chemical bond", we consider that the ΔE_a^* energy not only is made up from that part required to break all the bonds, ΔE_a^{*bonds}, but also includes a contribution ($\Delta E_{nb}^* = -E_{nb}^*$) required to annihilate all the nonbonded interactions. We write, accordingly, $\Delta E_a^* = \Delta E_a^{*bonds} - E^*_{nb}$ and treat the bonded part as a sum of energy terms ϵ_{ij} referring to the individual bonds ij, i.e.

$$\Delta E_a^* = \sum \epsilon_{ij} - E_{nb}^* \quad (11)$$

Using the exact quantum mechanical definition $\Delta E_a^* = \sum_k \langle \psi_k^{at} | H_k^{at} | \psi_k^{at} \rangle - \langle \psi^{mol} | H^{mol} | \psi^{mol} \rangle$, where H_k^{at} and H^{mol} are the appropriate Hamiltonians and ψ_k^{at} and ψ^{mol} the corresponding ground-state wave functions, we calculate the derivative $\partial \Delta E_a^*/\partial Z_k$ with respect to the nuclear charge Z_k of the kth atom in the molecule leaving the internuclear distances and the number of electrons unchanged. It follows from the Hellmann–Feynman theorem that[8]

$$V(k,\text{mol}) = V_{ne}(\text{free atom } k) - Z_k\, \partial \Delta E_a^*/\partial Z_k \quad (12)$$

The only terms contributing to the derivative $\partial \Delta E_a^*/\partial Z_k$ are those involving atom k, namely, its bonded interactions with atoms j and the nonbonded ones with all other atoms, giving $\partial \Delta E_a^*/\partial Z_k = \sum_j \partial \epsilon_{kj}/\partial Z_k - \partial E_{nb}^*/\partial Z_k$. Neglecting temporarily the nonbonded contributions, we deduce from eq 12 that

$$V(k,\text{mol}) \simeq V_{ne}(\text{free atom } k) - Z_k \sum_j \partial \epsilon_{kj}/\partial Z_k \quad (13)$$

This approximation for the "true" $V(k,\text{mol})$ potential is certainly valid when $|E_{nb}^*| \ll \Delta E_a^{*bonds}$. More appropriately, however, we regard this expression as a description of that portion of the total $V(k,\text{mol})$ which refers precisely to the bonded part of ΔE_a^*. We can thus safely proceed by using eq 13, just bearing in mind that the quantities derived therefrom refer to molecules stripped of their nonbonded interactions. In this sense, the validity of eq 13 is determined only by the validity of apportioning ΔE_a^* into bonded and nonbonded terms, i.e., ultimately, by the very existence of "chemical bonds".

With use of eq 4, as well as eq 2 and 13, in order to obtain the energy difference ΔE_k defined by eq 9, it is found that

$$\Delta E_k = K_k^{mol} Z_k \sum_j \partial \epsilon_{kj}/\partial Z_k + (K_k^{at} - K_k^{mol}) V_{ne}(\text{free atom } k) \quad (14)$$

thus stressing the role of local binding properties in determining ΔE_k. This equation translates the concept of a molecule viewed as a collection of chemical bonds into a description in terms of "atoms in a molecule". Namely, it appears that besides the small nonbonded contribution which evidently depends on the whole of the molecule, ΔE_k is primarily related both to the type and to the number of bonds formed by atom k.

For the alkanes, the appropriate parameters are[8] $K_C^{at} = 1/2.3390$, $K_C^{mol} = 1/2.3329$, and $K_H^{at} = K_H^{mol} = 1/2$. With V_{ne}(C,atom) = −88.4879 au, deduced from eq 2 by using the experimental energy of carbon[13] (−37.8315 au), eq 14 becomes $\Delta E_C = (6/2.3329)\sum_j \partial \epsilon_{Cj}/\partial Z_C + 0.099$ au. For the ethane CC and CH bonds, ab initio calculations lead to $\partial \epsilon_{CC}/\partial Z_C = 0.012$, $\partial \epsilon_{CH}/\partial Z_C = 0.027$, and $\partial \epsilon_{CH}/\partial Z_H = 0.153$ au (Appendix I), giving, for the *ethane* C and H atoms, $\Delta E_C = 0.338$ and $\Delta E_H = 0.0765$ au, respectively. With the assumption for a moment that the $\partial \epsilon_{kj}/\partial Z_k$ derivatives can be treated as constants, eq 14 suggests that $\Delta E_C = 0.377$ (methane C atom), 0.300 (secondary C), 0.261 (tertiary C), and 0.222 au (quaternary C). These results, which shall be commented upon further below, illustrate the "atoms in a molecule" aspect of the present theory.

The chemical bonds themselves are also well described by eq 14. Their energies are deduced by the following decomposition of ΔE_k among the bonds formed by atom k. First, the "extraction" from the host molecule of an atom i forming ν_i bonds requires an energy $(K_i^{at} - K_i^{mol})V_{ne}(\text{free atom } i)/\nu_i$ for each bond, meaning that for the cleavage of an ij bond this type of contribution must be counted once for both the i and j atoms. In addition, this atomization requires an energy $K_i^{mol} Z_i\, \partial \epsilon_{ij}/\partial Z_i$ for each bond formed by i, meaning that the cleavage of an ij bond involves this type of contribution for each bonded partner. Consequently, the portion of the total atomization energy associated with the ij bond is

$$\epsilon_{ij} = K_i^{mol} Z_i\, \partial \epsilon_{ij}/\partial Z_i + K_j^{mol} Z_j\, \partial \epsilon_{ij}/\partial Z_j + (K_i^{at} - K_i^{mol}) V_{ne}(\text{free atom } i)/\nu_i + (K_j^{at} - K_j^{mol}) V_{ne}(\text{free atom } j)/\nu_j \quad (15)$$

Inserting the appropriate parameters in eq 15, we obtain $\epsilon_{CC} = 69.8$ and $\epsilon_{CH} = 107.1$ kcal mol^{-1} (1 au = 627.51 kcal mol^{-1}) for the ethane bonds. (We postpone temporarily the question of how these values relate to the customary empirical ones, ~82 and ~105 kcal mol^{-1}, respectively.) This new energy formula, which is the explicit "chemical bond" counterpart of eq 14, illustrates clearly the equivalence of the models describing molecules in terms of atomic-like contributions or, alternatively, in terms of chemical bonds. In the case of ethane, for example, we write $\Delta E_a^*(\text{bonds}) = 2\Delta E_C(\text{prim}) + 6\Delta E_H = \epsilon_{CC} + 6\epsilon_{CH} = 712.3$ kcal mol^{-1}. While this result is reasonably close to the experimental one[14] (710.54 kcal mol^{-1}), we also observe that the result deduced for adamantane, $\Delta E_a^*(\text{bonds}) = 6\Delta E_C(\text{sec}) + 4\Delta E_C(\text{tert}) + 16\Delta E_H = 12\epsilon_{CC} + 16\epsilon_{CH} = 2551.2$ kcal mol^{-1}, is in error by ~137 kcal mol^{-1} with respect to the experimental value, 2688.05 kcal mol^{-1}.

This last example raises the obvious question about the origin of the discrepancies between observed and calculated atomization energies which are known to plague simple bond additivity schemes.[15] A pertinent reason can be found in the fact that nonbonded interactions are entirely neglected in these calculations. Leaving this subject temporarily, we examine now another major point concerning exclusively the bonded contributions.

First of all, we note that any sum $\sum \Delta E_k = \sum \epsilon_{ij}$ constructed, as we did, from a fixed set of ΔE_k or ϵ_{ij} values is a clear representation of exact additivity. The clue to the correct meaning of this sum lies in the precise definition of the derivatives $\partial \epsilon_{kj}/\partial Z_k$ which enter the calculation of the ΔE_k and ϵ_{ij} terms. These derivatives are, indeed, bound to the same conditions which apply in the present use of the Hellmann–Feynman theorem; namely, they are carried out leaving the internuclear distances and the number of electrons unchanged. The appropriate derivatives should, therefore, be calculated in each case of interest for the specified kj bond to which they refer, i.e., for a specified situation described by the kj internuclear distance and the electron distributions about the atoms involved. Instead, with the selection of a fixed set of $\partial \epsilon_{kj}/\partial Z_k$ values, we end up using "model" bonds

(13) Calculated as multiplet average from the ionization potentials given in: C. E. Moore, *Natl. Stand. Ref. Data Ser. (U.S. Natl. Bur. Stand.)*, **NSRDS-NBS 34** (1970).

(14) H. Henry, G. Kean, and S. Fliszár, *J. Am. Chem. Soc.*, **99**, 5889 (1977).

(15) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, 1970.

or "model" atoms (e.g., those of ethane in the example given above), disregarding possible changes in internuclear distances and electron populations. Now, the simple sum of constant bond (or atomic) terms, implying a fixed set of $\partial\epsilon_{kj}/\partial Z_k$ derivatives and, hence, invariant "local" electron populations, cannot (as a rule) describe an electroneutral molecule. Indeed, if *constant* electron populations N_A ($\neq Z_A$), N_B ($\neq Z_B$), ... are associated with all individual atoms, A, B, ... of an electroneutral molecule, any other nonisomeric molecule constructed from the same atoms with the same charges would not satisfy the charge normalization condition.[16]

Hence, unless one denies entirely the existence of charge transfers within molecules, this argument suffices to put any additivity scheme involving fixed $\partial\epsilon_{kj}/\partial Z_k$ derivatives on the disabled list. The discrepancies between observed and exactly "additive" energies cannot be explained on steric grounds alone. Rather, in the search of a satisfactory expression for the bonded contributions, we must explicitly include a charge dependence in the ϵ_{ij} (or ΔE_k) terms. In doing so we consider, as succinctly stated by Platt, that "a theory of chemistry and the chemical bond is primarily a theory of electron density".[17]

Charge Dependence of Chemical Binding. The bond energy terms ϵ_{ij} deduced from a well-defined reference set of $\partial\epsilon_{ij}/\partial Z_i$ values are, from here on, designated by ϵ^0_{ij}. The difference

$$-E(\text{charge}) = \Delta E_a{}^{*\text{bonds}} - \sum\epsilon^0_{ij} \tag{16}$$

measures the effect of using in each case the appropriate charge distributions, instead of frozen ones. The calculation of E(charge) is, in fact, one that relates the changes from ϵ^0_{ij} to ϵ_{ij} to changes in the electronic structures of atoms i and j. For small perturbations, the latter are considered to occur in the valence shells, leaving the core regions unaltered. The following calculations are carried out in the spirit of the Politzer–Parr electron partitioning into core and valence regions.[4] The nuclear charges Z_i^{eff} and Z_j^{eff} are effective charges; e.g., Z^{eff} (carbon) $\simeq$ 4 au. Similarly, electron densities (ρ), populations (N), and energies refer to the valence shells.

E(charge) is most conveniently derived from the change ΔV_{ne}(charge) in nuclear–electronic potential energy accompanying the appropriate charge normalization. This ΔV_{ne}(charge) correction, of course, concerns only the interactions between bonded atoms. When added to the sum $\sum_k V(k,\text{mol})$ obtained by using eq 13, the result differs from the exact one only by the omitted nonbonded contributions. Since the exact $\sum_k V(k,\text{mol})$ sum and the one derived from eq 13 both are to be multiplied by $K_{\text{Av}}{}^{\text{mol}}$ to give the corresponding molecular energies (i.e., respectively the total one and that of no charge normalized molecules stripped of their nonbonded contributions), it appears safe to write[18]

$$E(\text{charge}) = K_{\text{Av}}{}^{\text{mol}}\Delta V_{\text{ne}}(\text{charge}) \tag{17}$$

The problem of calculating E(charge) thus reduces to a calculation of nuclear–electronic potential energies. The contribution to ΔV_{ne}(charge) involving Z_i^{eff} consists, first, of its interaction with the electrons of atom i

$$-Z_i^{\text{eff}}\int_{\tau_i}\frac{1}{|\mathbf{r}-\mathbf{r}_i|}\rho_i(\mathbf{r})\,d\mathbf{r}$$

where the integration is carried out over the volume τ_i containing the N_i electrons allocated to atom i, and, second, of a part

$$-Z_i^{\text{eff}}\int_{\tau_j}\frac{1}{|\mathbf{r}-\mathbf{r}_i|}\rho_j(\mathbf{r})\,d\mathbf{r}$$

referring to the interaction with the N_j electrons of each atom j bonded to i. The above integrals are conveniently written as $\int(1/|\mathbf{r}-\mathbf{r}_i|)\rho_i\,d\mathbf{r} = N_i\langle r_i^{-1}\rangle$ and $\int(1/|\mathbf{r}-\mathbf{r}_i|)\rho_j\,d\mathbf{r} = N_j\langle r_{ij}^{-1}\rangle$, where $\langle r_i^{-1}\rangle$ and $\langle r_{ij}^{-1}\rangle$ are respectively the average inverse distances from Z_i^{eff} to N_i and N_j. Similar expressions are written for the reference molecule with atomic electron populations N^0_i, N^0_j and average inverse distances $\langle r_i^{-1}\rangle^0$, $\langle r_{ij}^{-1}\rangle^0$. In this manner we avoid the explicit calculation of the electron densities ρ and, moreover, postpone the precise definition of the appropriate N_i's, i.e., the problem of electron partitioning. The molecular ΔV_{ne}(charge) correction is then simply given by eq 18.

$$\Delta V_{\text{ne}}(\text{charge}) = -\sum_i Z_i^{\text{eff}}[N_i\langle r_i^{-1}\rangle - N^0_i\langle r_i^{-1}\rangle^0 + \sum_j(N_j\langle r_{ij}^{-1}\rangle - N^0_j\langle r_{ij}^{-1}\rangle^0)] \tag{18}$$

At this stage we introduce the approximation (19) which implies

$$\langle r_{ij}^{-1}\rangle = \langle r_{ij}^{-1}\rangle^0 \tag{19}$$

that small perturbations in the electron populations do not affect their shape, i.e., their center of charge. For nearly spherical atomic charge clouds, we approximate $\langle r_{ij}^{-1}\rangle^0$ by the inverse of the internuclear distance $(r_{ij}^{-1})_{nn}$. The $(r_{ij}^{-1})_{nn}$'s are temporarily kept constant in comparisons between bonds of similar nature (e.g., the CC or the CH bonds in saturated hydrocarbons) because we are presently concerned only with the charge effects on the ϵ_{ij}'s. Defining now

$$N_i = N^0_i + \Delta N_i \tag{20}$$

it follows from eq 17–20 that

$$E(\text{charge}) = -K_{\text{Av}}{}^{\text{mol}}\sum_i Z_i^{\text{eff}}(N_i\langle r_i^{-1}\rangle - N^0_i\langle r_i^{-1}\rangle^0 + \sum_j\langle r_{ij}^{-1}\rangle^0\Delta N_j) \tag{21}$$

As for the difference $N_i\langle r_i^{-1}\rangle - N^0_i\langle r_i^{-1}\rangle^0$ appearing in eq 21, first, we expand $N_i\langle r_i^{-1}\rangle$ in a Taylor series (see eq 22), and, second,

$$N_i\langle r_i^{-1}\rangle = N^0_i\langle r_i^{-1}\rangle^0 + \left(\frac{\partial N_i\langle r_i^{-1}\rangle}{\partial N_i}\right)^0\Delta N_i + \frac{1}{2!}\left(\frac{\partial^2 N_i\langle r_i^{-1}\rangle}{\partial N_i^2}\right)^0(\Delta N_i)^2 + \ldots \tag{22}$$

define the energy (see eq 23) of atom i in its valence state, in the

$$E_i^{\text{vs}} = -K_i^{\text{mol}}Z_i^{\text{eff}}N_i\langle r_i^{-1}\rangle \tag{23}$$

current acceptation of this term, chosen so as to have as nearly as possible the interaction of the electrons of the atom with one another, as they have when the atom is part of a molecule. The valence state is considered as being formed from a molecule by removing from one atom all the other atoms without allowing any electronic rearrangement and differs, hence, from the energy given by eq 4 by the noninclusion of the electronic and nuclear interactions due to the other atoms of the molecule. Taking now the successive derivatives of E_i^{vs} (eq 23) evaluated for $N_i = N^0_i$, i.e., $(\partial E_i^{\text{vs}}/\partial N_i)^0 = -K_i^{\text{mol}}Z_i^{\text{eff}}(\partial N_i\langle r_i^{-1}\rangle/\partial N_i)^0$ etc., we obtain, from eq 22, that

$$N_i\langle r_i^{-1}\rangle - N^0_i\langle r_i^{-1}\rangle^0 = -\frac{1}{K_i^{\text{mol}}Z_i^{\text{eff}}}\left[\left(\frac{\partial E_i^{\text{vs}}}{\partial N_i}\right)^0\Delta N_i + \frac{1}{2!}\left(\frac{\partial^2 E_i^{\text{vs}}}{\partial N_i^2}\right)^0(\Delta N_i)^2 + \ldots\right]$$

and, from eq 21, that

$$E(\text{charge}) = K_{\text{Av}}{}^{\text{mol}}\sum_i\left[\frac{1}{K_i^{\text{mol}}}\left(\frac{\partial E_i^{\text{vs}}}{\partial N_i}\right)^0\Delta N_i + \frac{1}{2!K_i^{\text{mol}}}\left(\frac{\partial^2 E_i^{\text{vs}}}{\partial N_i^2}\right)^0(\Delta N_i)^2 + \ldots - Z_i^{\text{eff}}\sum_j\langle r_{ij}^{-1}\rangle^0\Delta N_j\right] \tag{24}$$

Finally, when the result is now expressed in terms of net (i.e., nuclear minus electronic) charges

(16) For example, if in ethane the C and H net charges are 0.0351 and −0.0117 e, respectively, a $C_{10}H_{16}$ hydrocarbon constructed from these atoms would be electron deficient by 0.1638 e.

(17) J. R. Platt, *Handb. Phys.*, **371c**, 188 (1961).

(18) A similar but less refined analysis, based on a model of "pseudodiatomic molecules", is given in S. Fliszár, *J. Chem. Phys.*, **71**, 700 (1979).

$$\Delta q = -\Delta N$$

it follows from eq 16 that, to a first order in Δq

$$\Delta E_a^{*\text{bonds}} = \sum \epsilon^0_{ij} + K_{\text{Av}}^{\text{mol}} \sum_i \left[\frac{1}{K_i^{\text{mol}}} \left(\frac{\partial E_i^{\text{vs}}}{\partial N_i} \right)^0 \Delta q_i - Z_i^{\text{eff}} \sum_j \langle r_{ij}^{-1} \rangle^0 \Delta q_j \right] \quad (25)$$

This equation contains the full information about the effect of atomic charges in determining $\Delta E_a^{*\text{bonds}}$ energies, showing, namely, that isomers or conformers differing in their electron distributions differ in the overall stability of their chemical bonds.

A complete description of $\Delta E_a^{*\text{bonds}}$ should also allow for changes in internuclear distances. Including now the corresponding $V_{\text{nn}} - V^0_{\text{nn}}$ term into the sum $\sum_i \sum_j Z_i^{\text{eff}}(N_j \langle r_{ij}^{-1} \rangle - N^0_j \langle r_{ij}^{-1} \rangle^0)$ appearing in eq 18, we evaluate the new sum $\sum_i \sum_j Z_i^{\text{eff}} Z_j^{\text{eff}} [(r_{ij}^{-1})_{\text{nn}} - (r_{ij}^{-1})^0_{\text{nn}}] - Z_i^{\text{eff}} N_j \langle r_{ij}^{-1} \rangle + Z_i^{\text{eff}} N^0_j \langle r_i^{-1} \rangle^0$ by using the definition $Z_j^{\text{eff}} - N^0_j = q^0_j$ of net atomic charges. Comparison with eq 25 indicates then that the missing term in this expression is

$$K_{\text{Av}}^{\text{mol}} \sum_i \sum_j Z_i^{\text{eff}} Z_j^{\text{eff}} [(r_{ij}^{-1})_{\text{nn}} - (r_{ij}^{-1})^0_{\text{nn}} - (\langle r_{ij}^{-1} \rangle - \langle r_{ij}^{-1} \rangle^0)] + Z_i^{\text{eff}} q^0_j (\langle r_{ij}^{-1} \rangle - \langle r_{ij}^{-1} \rangle^\circ) \quad (26)$$

which represents the contribution to $\Delta E_a^{*\text{bonds}}$ due to variations in internuclear distances and to changes of electronic centers of charge. Without minimizing, in the more general case, the role of this type of contribution, we now focus attention on the term arising from charge renormalization, eq 25.

An enlightening result can, indeed, be derived from eq 25 by observing that the sum over all atoms i can be rearranged into an equivalent one involving individual bond contributions, giving for each ij bond

$$\epsilon_{ij} = \epsilon^0_{ij} + a_{ij} \Delta q_i + a_{ji} \Delta q_j \quad (27)$$

where

$$a_{ij} = \frac{1}{\nu_i} \frac{K_{\text{Av}}^{\text{mol}}}{K_i^{\text{mol}}} \left(\frac{\partial E_i^{\text{vs}}}{\partial N_i} \right)^0 - K_{\text{Av}}^{\text{mol}} Z_j^{\text{eff}} \langle r_{ij}^{-1} \rangle^0 \quad (28)$$

with ν_i = the number of bonds formed by atom i. The sum over all the bonds is then

$$\Delta E_a^{*\text{bonds}} = \sum \epsilon^0_{ij} + \sum_i \sum_j a_{ij} \Delta q_i \quad (29)$$

The proof follows from the sum $\Delta E_a^{*\text{bonds}} = \sum \epsilon_{ij}$ which yields eq 25. Of course, if desired, higher order derivatives of E_i^{vs} (from eq 24) and appropriate bond contributions from 26 can also be incorporated in the a_{ij}'s. The forthcoming numerical applications to saturated hydrocarbons reveal, however, that these second order corrections can be safely ignored as the results derived from the approximations 27 and 28 are well within experimental uncertainties.

Numerical Applications

Detailed numerical verifications of eq 5 and 7 were presented earlier[6-8,12] for numerous compounds, mainly at the level of Hartree–Fock calculations. The ultimate fine tuning provided by eq 27–29 now enables comparisons to be made at the level of experimental accuracy. This test is presented for saturated hydrocarbons $C_nH_{2n+2-2m}$ containing m ($\geq$0) six-membered rings, which is presently the only class of compounds for which we possess sufficient experimental results, namely, the thermochemical and spectroscopic data required for deducing the ΔE_a^*'s,[14] and comprehensive information about atomic charges[18-20] and nonbonded interactions.[22]

(19) S. Fliszār, G. Kean, and R. Macaulay, *J. Am. Chem. Soc.*, **96**, 4353 (1974).

(20) S. Fliszār, A. Goursot, and H. Dugas, *J. Am. Chem. Soc.*, **96**, 4358 (1974).

(21) S. Fliszār, *Can. J. Chem.*, **54**, 2839 (1976).

(22) S. Fliszār and M. T. Bēraldin, *Can. J. Chem.*, **57**, 1772 (1979).

As for the latter, Del Re[23] has shown that a valid approximation in σ systems is Coulombic in nature, i.e.

$$E_{\text{nb}}^* = \frac{1}{2} \sum_{k,l}^{\text{nb}} \frac{q_k q_l}{r_{kl}}$$

where q_k and q_l are the net atomic charges of nonbonded atom pairs at a distance r_{kl}. Numerical evaluations were presented earlier[22] with reference to a standard charge $q^0_C = q_C$(ethane) taken at 0.0694 e. Here we consider a description of E_{nb}^* by means of these numerical coulomb energies multiplied by a factor $(q^0_C/0.0694)^2$, q^0_C being now the "true" but still unknown net charge of the ethane carbon atom.

A convenient way for deducing the Δq_C's of eq 27 is offered by the remarkably accurate empirical relationship[20,21] (30) between

$$\delta_C = -237.1 \Delta q_C / q^0_C \quad (30)$$

carbon-13 nuclear magnetic resonance shifts relative to the ethane C atom and carbon net atomic charges. Of course, one can do without eq 30 and use only ab initio results. There is, however, no real point in not taking advantage of this relationship, just for the sake of "theoretical purity", since the charges obtained from the two methods agree within ~0.15% for the class of compounds investigated here. The adequacy of the charges obtained from eq 30 for the problem at hand is discussed in Appendix II.

We now direct our attention to the calculation of the a_{ij}'s (eq 28). The $\partial E_i^{\text{vs}}/\partial N_i$ derivatives are conveniently obtained from SCF-Xα theory.[24] For hydrogen we have used the α value (0.686) appropriate for partially negative H (like that of ethane) and which reproduces correctly its electron affinity.[25] For N_H = 1.0117 e (corresponding to q^0_C = 0.0351 e), it is found that $\partial E_H/\partial N_H$ = −0.195 au. For the carbon atoms we have considered, first, that fully optimized ab initio studies of hydrocarbons indicate that any gain in electronic charge, with respect to the ethane carbon, occurs at the 2*s* level.[26] Second, GTO(9*s*5*p*/6*s*) → [5*s*3*p*/3*s*] calculations of methane and ethane, using Dunning's exponents[27] and optimum contraction vectors,[26] indicate 2*s* populations of 1.42–1.46 e. Finally, SCF-Xα calculations[25] indicate $\partial E/\partial N$ values of −20.49, −19.87, and −19.26 eV for 2*s* populations of 1.40, 1.45, and 1.50 e, respectively, by using the α = 0.75928 value given by Schwarz.[28] These results suggest that the appropriate $\partial E_C^{\text{vs}}/\partial N_C$ derivative can be reasonably estimated at −0.735 au (−20 eV).

Turning now to the other terms appearing in eq 28, we approximate K_C^{mol} and $K_{\text{Av}}^{\text{mol}}$ by $^3/_7$ and use $K_H^{\text{mol}} = {}^1/_2$, as explained in the theoretical section leading to the Politzer approximation (eq 8). The $\langle r_{ij}^{-1} \rangle^0$ terms are taken at 1.53 and 1.08 Å for the CC and CH bonds, respectively. By means of these approximations, we deduce the following a_{ij} values from eq 28:

$$a_{CC} = -0.777 \text{ au} \qquad a_{CH} = -0.394 \text{ au} \qquad a_{HC} = -1.007 \text{ au} \quad (31)$$

At this stage, the required parameters being determined, we are ready to proceed with the master formula, eq 29, and study the $C_nH_{2n+2-2m}$ hydrocarbons. When the ethane CC and CH bonds are chosen as reference bonds, eq 29 takes the form

$$\Delta E_a^{*\text{bonds}} = (n - 1 + m)\epsilon^0_{CC} + (2n + 2 - 2m)\epsilon^0_{CH} + a_{CC} \sum N_{CC} \Delta q_C + a_{CH} \sum N_{CH} \Delta q_C + a_{HC} \sum \Delta q_H$$

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(26) G. Kean, M.Sc. Thesis, Université de Montréal, Montréal, 1974.

(27) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

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Table I. Comparison between Calculated and Experimental Atomization Energies (kcal/mol)[a]

no.	molecule	$\Sigma\epsilon_{ij}$(appar)	$\lambda_1\Sigma N_{CC}\delta_C + \lambda_2\Sigma\delta_C$	$-E_{nb}$*	ΔE_a* calcd	ΔE_a* exptl
1	methane	419.83	−0.39	−0.09	419.35	419.24
2	ethane	710.47	0.00	0.07	710.54	710.54
3	propane	1001.11	2.98	0.20	1004.29	1004.07
4	butane	1291.75	6.03	0.32	1298.10	1298.15
5	isobutane	1291.75	7.99	0.28	1300.02	1299.70
6	pentane	1582.39	9.07	0.44	1591.90	1592.20
7	isopentane	1582.39	10.39	0.39	1593.17	1593.43
8	neopentane	1582.39	13.36	0.32	1596.07	1595.94
9	hexane	1873.03	12.11	0.55	1885.69	1885.95
10	2-methylpentane	1873.03	13.48	0.50	1887.01	1886.86
11	3-methylpentane	1873.03	12.81	0.50	1886.33	1886.27
12	2,2-dimethylbutane	1873.03	14.96	0.43	1888.42	1888.86
13	2,3-dimethylbutane	1873.03	13.75	0.39	1887.17	1887.14
14	2,2,3-trimethylbutane	2163.67	18.03	0.46	2182.16	2181.90
15	cyclohexane	1743.84	16.23	0.73	1760.81	1760.82
16	methylcyclohexane	2034.48	21.43	0.83	2056.74	2057.13
17	*trans*-decalin	2777.20	37.11	1.26	2815.57	2815.50
18	adamantane	2648.02	38.68	1.31	2688.01	2688.05
19	bicyclo[2.2.2]octane	2195.92	21.58	1.03	2218.53	2218.40
20	1,1-dimethylcyclohexane	2326.51	24.12		2350.63	2351.1
21	ethylcyclohexane	2326.51	23.74		2350.25	2350.1
22	*n*-butylcyclohexane	2908.14	29.38		2937.52	2937.9
23	1,2-dimethyl-*trans*-cyclohexane	2326.51	26.04		2352.55	2351.9
24	1,2-dimethyl-*cis*-cyclohexane	2326.51	21.77		2348.28	2348.1
25	1,3-dimethyl-*cis*-cyclohexane	2326.51	26.40		2352.91	2353.0
26	1,3-dimethyl-*trans*-cyclohexane	2326.51	22.73		2349.24	2349.2
27	1,4-dimethyl-*trans*-cyclohexane	2326.51	26.38		2352.89	2353.0
28	1,4-dimethyl-*cis*-cyclohexane	2326.51	22.74		2349.25	2349.2
29	1-*cis*-3-*cis*-5-trimethylcyclohexane	2617.33	31.67		2649.00	2649.2
30	1-*cis*-3-*trans*-5-trimethylcyclohexane	2617.33	27.79		2645.11	2645.2
31	diamantane	3555.75	59.84		3615.59	3616.0

[a] The sum $\Sigma\epsilon_{ij}$(appar) was calculated for compounds 1-19 as $(1-m)\Delta E_a{}^{*\text{bonds}}(2) + (n-2+2m)[\Delta E_a{}^{*\text{bonds}}(1) - 7.4\lambda_2]$ (eq 33), which is also the result obtained from eq 32 with ϵ_{CC}(apparent) = $\epsilon^\circ_{CC} - a_{HC}q^\circ_C/2$ = 80.723 and ϵ°_{CH}(apparent) = $\epsilon^\circ_{CH} - a^\circ_{HC}q_H/4$ = 104.958 kcal/mol. The charge-dependent part was calculated by using λ_1 = 0.0356 and λ_2 = 0.0529. Details about the thermochemical and ^{13}C NMR data are given in ref 14. Compounds **20-31** were calculated by means of eq 35, using the parameters deduced from 1-20, *i.e.*, in kcal/mol, $\Delta E_a{}^*(2) - \Delta E_a{}^*(1) - 7.4\lambda_2$ = 290.814, λ_1 = 0.03244, and λ_2 = 0.05728. The experimental results selected for the test involving the empirical λ_2/λ_1 ratio are those of compounds 1-4, 8-11, **15**, and 17-19.

where N_{CC} and $N_{CH} = 4 - N_{CC}$ are respectively the number of CC and CH bonds formed by the C atom whose charge increment is Δq_C. Noting that $\sum\Delta q_H = -\sum\Delta q_C - nq^0{}_C - (2n + 2 - 2m)q^0{}_H$ (which follows from $\sum q_H = -\sum q_C$) and observing that $nq^0{}_C + (2n + 2 - 2m)q^0{}_H = (n - 1 + m)q^0{}_C/2 + (2n + 2 - 2m)q^0{}_H/4$ (which follows from $q^0{}_C + 3q^0{}_H = 0$), it is found that

$$\Delta E_a{}^{*\text{bonds}} = (n - 1 + m)(\epsilon^0{}_{CC} - a_{HC}q^0{}_C/2) + (2n + 2 - 2m)(\epsilon^0{}_{CH} - a_{HC}q^0{}_H/4) + \lambda_1\sum N_{CC}\Delta q_C + \lambda_2\sum\Delta q_C \quad (32)$$

where $\lambda_1 = a_{CC} - a_{CH}$ and $\lambda_2 = 4a_{CH} - a_{HC}$. Moreover, solving this equation for ethane, we obtain $\Delta E_a{}^{*\text{bonds}} = \epsilon^0{}_{CC} + 6\epsilon^0{}_{CH}$ and, similarly, for methane $\Delta E_a{}^{*\text{bonds}}{}_{(1)} = 4\epsilon^0{}_{CH} + a_{HC}q^0{}_C/3 + \lambda_2\Delta q_C(1)$, where $\Delta q_C(1) = q_C(CH_4) - q^0{}_C$. In this fashion we deduce from eq 30 and 32 that

$$\Delta E_a{}^{*\text{bonds}} = (1 - m)\Delta E_a{}^{*\text{bonds}}{}_{(2)} + (n - 2 + 2m)[\Delta E_a{}^{*\text{bonds}}{}_{(2)} - \Delta E_a{}^{*\text{bonds}}{}_{(1)}] + \lambda_1\sum N_{CC}\delta_C + \lambda_2[(n - 2 + 2m)\delta_C(CH_4) + \sum\delta_C] \quad (33)$$

where $\delta_C(CH_4)$ = −7.4 ppm from ethane. Equations 32 and 33 are the most convenient ones for deriving the $\Delta E_a{}^{*\text{bonds}}$ energies of the hydrocarbons under study.

A valid test for our theory is offered by the comparison of the empirical λ_2/λ_1 = 1.48 ratio, deduced (eq 33) from selected "most reliable" experimental ΔE_a* results, with its theoretical counterpart:

$$\frac{4a_{CH} - a_{HC}}{a_{CC} - a_{CH}} = \frac{(\partial E_C{}^{vs}/\partial N_C) - (6/7)(\partial E_H/\partial N_H)}{(-3/7)(Z_C{}^{\text{eff}}\langle r_{CC}{}^{-1}\rangle^0 - Z_H{}^{\text{eff}}\langle r_{CH}{}^{-1}\rangle^0)} = 1.49$$

Indeed, the empirical ratio calculated using E_{nb}* energies for $q^0{}_C$ in the neighborhood of 35 × 10^{-3} e is nearly independent of $q^0{}_C$, and so is the theoretical ratio in which only the derivatives are slightly affected by the particular choice for $q^0{}_C$. The appropriate $q^0{}_C$ value can be evaluated by rearranging eq 32 and 33 to give

$$2n\epsilon^0{}_{CC} = \Delta E_a{}^{*\text{bonds}} + n[\Delta E_a{}^{*\text{bonds}}{}_{(2)} - 2\Delta E_a{}^{*\text{bonds}}{}_{(1)} + 2\lambda_2\delta_C(1) + a_{HC}q^0{}_C] + (1 - m)[\Delta E_a{}^{*\text{bonds}}{}_{(2)} - 2\Delta E_a{}^{*\text{bonds}}{}_{(1)} + 2\lambda_2\delta_C(1)] - \lambda_1\sum N_{CC}\delta_C - \lambda_2\sum\delta_C \quad (34)$$

and by taking advantage of the fact that $\epsilon^0{}_{CC}$ is constant by definition. Using now the theoretical a_{ij}'s (eq 31), we write, in kcal mol^{-1} ppm^{-1}, $\lambda_1 = 0.383(627.51/237.1)q^0{}_C$ and $\lambda_2 = 0.569(627.51/237.1)q^0{}_C$ and find that for $q^0{}_C \simeq 0.035$ e, $\epsilon^0{}_{CC}$ remains constant at ~67.7 kcal/mol within the limits set by experimental uncertainties. Our optimum choice, $q^0{}_C$ = 0.0351 e, yields λ_1 = 0.0356 and λ_2 = 0.0529 kcal mol^{-1} ppm^{-1}. While this choice (as, for that matter, the precise conditions having led to the a_{ij} values given in eq 31) remains open to discussion, we feel presently unable to go beyond the present level of sophistication, precisely because of the uncertainties affecting experimental results and the evaluation of nonbonded interactions.

Examination of the results derived from eq 33 (Table I) indicates, indeed, that the agreement between calculated and experimental ΔE_a* atomization energies could hardly be any better, the average deviation (0.16 kcal/mol) being well within experimental uncertainties.

An equally good agreement is, of course, also obtained by using eq 32, with $\epsilon^0{}_{CC} - a_{HC}q^0{}_C/2$ = 80.723 and $\epsilon^0{}_{CH} - a_{HC}q^0{}_H/4$ = 104.958 kcal mol^{-1}. It is noteworthy that the $\epsilon^0{}_{CH}$ = 106.81 and $\epsilon^0{}_{CC}$ = 69.63 kcal mol^{-1} values derived in this manner fully confirm the corresponding theoretical ones from eq 15, i.e., 107.1 and 69.8 kcal mol^{-1}, respectively. Moreover, the above ~80.7 and ~105 kcal mol^{-1} figures closely resemble those deduced in empirical fashion by Allen[29] (82.31 and 104.73 kcal mol^{-1}, for ethane), which is also a satisfactory result. It is now clear, however, that the ~80.7 and ~105 values do *not* represent true CC and CH bond energies but only "apparent" ones, because of the involvement of the $a_{HC}q^0_C/2$ and $a_{HC}q^0_H/4$ terms. The correct meaning of empirical "apparent" bond energies can be inferred from eq 32 which, indeed, reduces formally to a simple bond additivity scheme, respecting electroneutrality, provided all Δq_C's are set equal to 0.

The results presented in Table I show that the largest part by far of the atomization energies is contributed by the "bonded" energy terms, leaving only a minor part to nonbonded interactions. Clearly, because of their smallness and relative insensitivity to structural features, nonbonded contributions cannot be regarded as being the leading terms in the explanation of energetic effects related to structural changes. Under these circumstances, taking advantage of the fact that nonbonded interactions behave, in general, in a "quasi-additive" fashion,[22] $E_{nb}^* = (1 - m)E_{nb}^*(C_2H_6) + (n - 2 + 2m)[E_{nb}^*(C_2H_6) - E_{nb}^*(CH_4)]$ and using eq 33, we obtain the useful approximation (35).

$$\Delta E_a^* = (1 - m)\Delta E_a^*(2) + (n - 2 + 2m)[\Delta E_a^*(2) - \Delta E_a^*(1)] + \lambda_1 \sum N_{CC}\delta_C + \lambda_2[(n - 2 + 2m)(-7.4) + \sum \delta_C] \tag{35}$$

Not surprisingly, the parameters ($\lambda_1 = 0.03244$ and $\lambda_2 = 0.05728$) determined empirically by using eq 35 differ slightly from the theoretical ones referring to $\Delta E_a^{*\text{bonds}}$. The comparison with experimental results[14] reveals an excellent agreement (0.23 kcal/mol average deviation) and supports the use of eq 35 for calculating ΔE_a^* energies.

Conclusions

The calculation of molecular energies is greatly facilitated by a separation of atomization energies into nonbonded and bonded contributions and by considering the latter as a sum of individual bond energy terms. In this perspective, the exact quantum mechanical formulation of atomic and molecular energies and the postulate that "chemical bonds" exist combine to show that the portion of the total molecular atomization energy associated with a bond formed by atoms i and j (i.e., the "bond energy" ϵ_{ij}) can be expressed in terms of the derivatives $\partial\epsilon_{ij}/\partial Z_i$ and $\partial\epsilon_{ij}/\partial Z_j$, where Z_i and Z_j are the nuclear charges of atoms i and j (eq 15). For ethane, taken as reference, the CC and CH bond energies are $\epsilon^0_{CC} = 69.63$ and $\epsilon^0_{CH} = 106.81$ kcal/mol, respectively.

When applied to saturated hydrocarbons, $C_nH_{2n+2-2m}$, the sum (number of CC bonds)ϵ^0_{CC} + (number of CH bonds)ϵ^0_{CH} = $(n - 1 + m)\epsilon^0_{CC} + (2n + 2 - 2m)\epsilon^0_{CH}$ gives disastrous results for the "bonded part", $\Delta E_a^{*\text{bonds}}$, of the atomization energy of all hydrocarbons other than ethane. The reason is of fundamental interest. Indeed, the definition of constant CC and CH bond energy terms implies an a priori selection of well-defined (constant) $\partial\epsilon_{ij}/\partial Z_i$ derivatives (e.g., those of the ethane CC and CH bonds, to give the above ϵ^0_{CC} and ϵ^0_{CH} values). Now, these derivatives are carried out under the precise conditions that the internuclear distances and the electron distributions are kept constant. Hence, the transfer of constant CC and CH bond energy terms from one molecule to another implies, ultimately, the construction of molecules using "atoms" having the same electron populations as in the molecule of reference. The important point is that this would not result in giving electroneutral molecules unless, of course, one denies any form of intramolecular charge transfer. For example, using the carbon and hydrogen "atoms" of ethane with net charges of 0.0351 and −0.0117 e, respectively, one obtains a methane "molecule" carrying an excess electronic charge of −0.0117 e. Consequently, before the failure of simple bond additivity schemes involving constant bond terms is blamed on "steric effects" of whatever nature, the first step to be made is to ensure electroneutrality of the molecules by restoring the appropriate electron distributions. From there on, the theory of the chemical bond becomes a theory of electron density.

Indeed, a token charge renormalization assuming constant atomic charges at the carbon atoms and letting the hydrogen atoms pick up whatever is necessary to maintain electroneutrality results in a scheme which is formally bond additive, with theoretical "apparent" CC and CH contribution of ~80.7 and ~105 kcal mol^{-1}, respectively. This result is worth mentioning because it explains the origin of this sort of numerical values from empirical correlations and the fallacy underlying them.

Actual molecules, of course, ensure their electroneutrality simply by allowing all atomic charges to assume their proper values, which are reflections of the appropriate molecular wave functions. In that event, the CC and CH bond energy terms are (in kcal/mol)

$$\epsilon_{CC} = 69.63 + a_{CC}\Delta q_C(\text{atom } i) + a_{CC}\Delta q_C(\text{atom } j)$$

$$\epsilon_{CH} = 106.81 + a_{CH}\Delta q_C + a_{HC}\Delta q_H$$

where Δq_C and Δq_H represent the increments in net atomic charges at the carbon and hydrogen atoms, with respect to the ethane C and H net charges. A negative Δq_C or Δq_H value corresponds to an actual increase of electron population at C or H. The a_{CC}, a_{CH}, and a_{HC} coefficients, which were derived theoretically (eq 28 and 31), are negative. Consequently, any increase in electronic charge at the bond forming atoms leads to larger bond energies, which is a stabilizing effect.

The detailed features of these bond stabilizing effects by electronic charges are most interesting. For convenience, we express here the a_{ij}'s (eq 31) in kcal mol^{-1} me^{-1} units, referring, hence, to charge increments of one millielectron (1 me = 10^{-3} e), i.e., $a_{CC} = -0.488$, $a_{CH} = -0.247$, and $a_{HC} = -0.632$. This means that addition of 1 me to hydrogen ($\Delta q_H = -1$ me) stabilizes a CH bond by 0.632 kcal/mol, whereas 1 me electronic charge added to carbon has a stabilizing effect of 0.247 kcal/mol on a CH bond and of 0.488 kcal/mol on a CC bond. For the saturated hydrocarbons under study, these simple rules describe the largest part by far of all the effects which govern molecular stabilities and differentiate isomers or conformers from one another.

Let us examine a few examples and consider, to begin with, a C_β–C_α–H fragment. The transfer of 1 me from the hydrogen to the adjacent α-carbon destabilizes the CH bond by 0.632 − 0.247 = 0.385 kcal/mol and stabilizes the C_α–C_β bond by 0.488 kcal/mol. The net gain in stabilization is thus 0.488 − 0.385 = 0.103 kcal/mol for this fragment. Had the transfer occurred to the β carbon, the C_α–H bond would have been destabilized by 0.632 and C_α–C_β stabilized by 0.488 kcal/mol. Moreover, additional C_β–H or C_β–C would have been stabilized by 0.247, viz., 0.488 kcal/mol. It follows therefrom that any electron enrichment on carbon atoms at the expense of electron populations at the hydrogen atoms results in a gain in molecular stability. This rule expresses, in a nutshell, the nature of the prime factors governing molecular stabilities. In comparisons between isomers or conformers, the more stable form has, on the whole, somewhat "weaker" CH bonds, which is largely compensated by the stabilization of the carbon skeleton. A detailed "bond by bond" calculation along these lines is presented in Appendix III, showing that the chair form of cyclohexane is 5.39 kcal/mol more stable than its boat conformer.

At some point, we mentioned that "steric effects" would be discussed. It is clear that individual nonbonded interactions of the q_kq_l/r_{kl} type may occasionally be fairly important, e.g., ~0.07 kcal/mol between two H atoms in methane. Because the interactions between net charges of the same sign are positive while the others are negative, a near cancellation of all the effects occurs at the molecular level (Table I) so that, finally, there is not much left for discussion. This is just as fine, because our analysis shows that the factors explaining the stereochemical effects are essentially contained in the description of the charge-dependent part of the bond energies, leaving only a very minor place to "steric" nonbonded interactions, "ring strain", or things of that sort. (The situation may, of course, be different in other classes of compounds.)

Indeed, the most convenient way of deducing atomization energies of saturated hydrocarbons is offered by eq 35, which includes, in an approximate way, the major part of the nonbonded

(29) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).

term. At this stage, finally, it is worth remembering that these $\Delta E_a{}^*$ energies refer to molecules in their hypothetical vibrationless state, at 0 K. The role of vibrational energies in determining molecular stabilities is dealt with in a forthcoming paper.

The present numerical analyses have involved saturated hydrocarbons, which are interesting in their own right, essentially because of the large body of experimental evidence accumulated in that area. The success of our approach justifies the hope that studies concerning other, presumably σ, systems may profit from the present theory. While (for the time being) eq 15 is difficult to apply at the level of experimental accuracy, it seems reasonable to anticipate, on the other hand, that an adequate knowledge can be gained about the important charge effects on bond energies, because this information can be derived from the appropriate a_{ij}'s (eq 28). On the whole, the present results are encouraging because they offer, in the simplest possible way, a clear link between molecular energies and charge distributions.

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Appendix I

The $\partial\epsilon_{kj}/\partial Z_k$ derivatives were deduced from eq 13 by assuming $E_C = -37.8315$ au (multiplet average)[13] and, hence, V_{ne}(free atom C) = 2.3390(−37.8315) = −88.4879 au. The theoretical results were obtained from GTO($9s5p/6s$) → [$5s3p/3s$] calculations by using Dunning's exponents[27] and optimum contraction vectors,[26] i.e., 42111 for C(s), 311 for C(p) and 222 for H(s), which yield the lowest molecular energies. The Phantom system of programs[30] was used.

The results obtained for methane, V_{ne}(C,mol) = −100.2656, V(C,mol) = −88.5368, V_{ne}(H,mol) = −4.9429, and V(H,mol) = −1.1129 au, were rescaled by using the experimental molecular energy (−40.4996 au) and the calculated $E_{mol}/(V_{ne} + 2V_{nn}) = 1/2.3139$ ratio with $V_{nn} = 13.5245$ au, giving an "experimental" $V_{ne} = -120.7610$ instead of the calculated one, $V_{ne} = -120.0372$ au. Therefrom we deduce the "corrected" values V_{ne}(C,mol) = −100.8702, V_{ne}(H,mol) = −4.9727, V(C,mol) = −89.1414, and V(H,mol) = −1.1427 au, giving (eq 13) $\partial\epsilon_{CH}/\partial Z_C = 0.027$ and $\partial\epsilon_{CH}/\partial Z_H = 0.143$ au. Considering that the C net charges in methane and ethane differ only by ~3% one from another,[19-21] we assume in the present approximation that this $\partial\epsilon_{CH}/\partial Z_C$ value applies also to the ethane CH bonds.

For ethane, we rescale the ab initio results V_{ne}(C,mol) = −114.0649, V(C,mol) = −88.4663, V_{ne}(H,mol) = −6.6770, and V(H,mol) = −1.1211 au by using the experimental molecular energy, −79.7953 au, and the calculated $E/(V_{ne} + 2V_{nn}) = 1/2.3187$ ratio, with $V_{nn} = 42.2663$ au, giving an "experimental" $V_{ne} = -269.5540$ instead of the calculated one, $V_{ne} = -268.1918$ au. The "corrected" values are, thus, V_{ne}(C,mol) = −114.6442, V_{ne}(H,mol) = −6.7100, V(C,mol) = −89.0458, and V(H,mol) = −1.1540, giving (eq 13) $\partial\epsilon_{CC}/\partial Z_C = 0.012$ and $\partial\epsilon_{CH}/\partial Z_H = 0.154$. From 6-31G calculations, we obtain virtually the same $\partial\epsilon_{CC}/\partial Z_C$ and $\partial\epsilon_{CH}/\partial Z_C$ results, but $\partial\epsilon_{CH}/\partial Z_H$ is now ~0.152 au.

This rescaling, involving corrections of the order of ~0.5%, is made to remain internally coherent with the detailed features of the ab initio results on which they are based and has the merit that the resulting molecular energies and their components are set on the same footing as the energies of the isolated atoms, which are taken at their experimental values. The overall coherence of our results can thus, as it should, be demonstrated at a level which is close to experimental accuracy. It is noteworthy that, when used in eq 15, these derivatives yield within ~0.3 kcal/mol the empirical ϵ_{ij} results. This suggests that nonbonded contributions are, indeed, small and that eq 13 represents a valid approximation for estimating the $\partial\epsilon_{kj}/\partial Z_k$ derivatives.

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Appendix II

Atomic charges are most conveniently extracted from molecular wave functions following Mulliken's population analysis.[31] This method implies the half-and-half partitioning of all overlap population terms among the centers k, l, ... involved. The problem of the division of the overlap charge has concerned many authors.[32] Indeed, while the usual half-and-half assignment is easy to defend in situations involving partners of equal nature, this may be a less good approximation in cases involving dissimilar atoms. Assuming now a modified mode of distributing overlap populations, one obtains for the population of center k, in standard notation

$$N(k) = 2\sum_i\sum_r\left(C^2_{ir_k} + \sum_{l\neq k} C_{ir_k}C_{is_l}S_{r_ks_l}\lambda_{r_ks_l}\right)$$

where the weighting factor $\lambda_{r_ks_l}$ causes the departure from the usual halving of the overlap terms. For saturated hydrocarbons, this leads to the useful approximations:[19-21] where $q_H{}^{\text{Mulliken}}$ and

$$q_H = q_H{}^{\text{Mulliken}} - p$$

$$q_C = q_C{}^{\text{Mulliken}} + N_{CH}p$$

$q_C{}^{\text{Mulliken}}$ are Mulliken's charges ($\lambda_{r_ks_l} = 1$), N_{CH} is the number of H atoms bonded to C, and p is the departure from the usual halving of the C–H overlap population, for one C–H bond.

The appropriate p for the problem at hand was determined as follows. Applying eq 27, in which $\Delta q_C = q_C - q_C$(ethane) and $\Delta q_H = q_H - q_H$(ethane), we have expressed q_C and q_H as indicated above by using Mulliken populations as input and leaving p as the unknown to be determined. The Mulliken charges were derived from fully optimized STO-3G calculations.[19,33] The $\Delta E_a{}^{*\text{bonds}}$'s constructed in this fashion (eq 32) were compared with their experimental counterparts, and p was determined by least-squares analysis. This procedure amounts to an experimental partitioning of overlap populations. For fully optimized STO-3G charges, we obtain $p = (30.3 \pm 0.3) \times 10^{-3}$ e. On the other hand, the same set of Mulliken charges, when compared to the corresponding ^{13}C NMR shifts,[20,21] yields $p = 30.12 \times 10^{-3}$ e and gives eq 30. Consequently, since the same definition of charge satisfies the appropriate equations for $\Delta E_a{}^{*\text{bonds}}$ and δ_C, we can use the latter (eq 30) for deriving the required Δq_C's.

Detailed studies[19,20] have shown that this sort of analysis holds independently of the LCAO–MO method selected for calculating Mulliken charges. However, while the ordering of the C net charges (i.e., q_C/q^0_C) is uniquely defined, we are presently unable to derive theoretically the reference net charge q^0_C in a satisfactory manner. The q^0_C's corresponding to STO-3G, $7s3p/3s$, and 6-31G calculations are 0.0694, 0.060, and 0.058 e, respectively, and that resulting from the present numerical analysis is 0.0351 e.

Appendix III

For the boat form of cyclohexane we have calculated δ 10.7 for carbons 1 and 4 and δ 16.5 (from ethane) for the other four C atoms, using Grant's parameters.[34] It follows from eq 30 that $\Delta q_C = -1.584$ me for carbons 1 and 4 and $\Delta q_C = -2.443$ me for the other C atoms. Each of the four CC bonds involving C-1 and C-4 is thus 0.488 (1.584 + 2.443) = 1.965 kcal/mol more stable than the ethane CC bond, and each of the remaining two CC bonds is more stable by 2.384 kcal/mol, meaning that the total gain in stability, relative to ethane CC bonds, is 12.63 kcal/mol. The atomic charges are 33.516 (C-1, -4) and 32.657 me (C-2, -3, -5, -6) for a total of 197.66 me on the carbon atoms and

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-16.472 me, on the average, for each H atom. The average $\Delta q_H = -4.772$ me value, while not giving a true reflection of the individual CH bonds, is sufficient for the correct evaluation of the total gain in stability of the CH part. Each of the four CH bonds formed by C-1 and C-4 is (in this "average" calculation) $1.584 \times 0.247 \pm 4.772 \times 0.632 = 3.407$ kcal/mol more stable than the ethane CH bond, and each of the other eight CH bonds has gained $2.443 \times 0.247 + 4.772 \times 0.632 = 3.169$ kcal/mol. The total stabilization is, hence, 12.63 (CC bonds) + 42.58 kcal/mol (CH bonds) with respect to the ethane bonds.

For the chair form of cyclohexane, we obtain from δ 21.8 (ppm from ethane) that $\Delta q_C = -3.227$, giving a stabilization of $2 \times 0.488 \times 3.227 = 3.150$ kcal/mol for each CC bond. The "average" charge on the H atoms being now -15.937 me and, thus, $\Delta q_H = -4.237$ me, each CH bond is stabilized by $4.237 \times 0.632 + 3.227 \times 0.247 = 3.475$ kcal/mol. The total gain in stability is, hence, 18.90 (CC bonds) + 41.70 kcal/mol (CH bonds) relative to the ethane bonds.

Finally, comparing now the boat and chair forms, it is deduced that the 12 CH bonds are more stable in the boat conformer by 0.88 kcal/mol but that the carbon skeleton of chair cyclohexane is more stable than that of the boat form by 6.27 kcal/mol, giving a total difference in stability of 5.39 kcal/mol favoring the chair conformer. This result agrees with the measured energy increment (5.39 kcal/mol) between the *trans-anti-trans-* and *trans-syn-trans*-perhydroanthracenes,[35] which differ only because of the center boat in the former compound, and with the difference in $\Delta E_a{}^{*\text{bonds}}$, 5.23 kcal/mol, calculated from their ^{13}C spectra[14] by using eq 33.

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Gas-Phase Ion/Molecule Isotope-Exchange Reactions: Methodology for Counting Hydrogen Atoms in Specific Organic Structural Environments by Chemical Ionization Mass Spectrometry

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Abstract: Ion/molecule reactions are described which facilitate exchange of hydrogens for deuteriums in a variety of different chemical environments. Aromatic hydrogens in alkylbenzenes, oxygenated benzenes, *m*-toluidine, *m*-phenylenediamine, thiophene, and several polycyclic aromatic hydrocarbons and metallocenes are exchanged under positive ion CI conditions by using either D_2O, EtOD, or ND_3 as the reagent gas. Aromatic hydrogens, benzylic hydrogens, and hydrogens on carbon adjacent to carbonyl groups suffer exchange under negative ion CI conditions in ND_3, D_2O, and EtOD, respectively. A possible mechanism for the exchange process is discussed.

Introduction

Solution methods of exchanging hydrogen for deuterium in organic molecules have been widely used in structural studies involving mass spectrometry.[1,2] Hunt and co-workers[3] developed a simplified procedure for replacing acidic hydrogens with deuterium under CI conditions by using deuterium oxide as the reagent gas. Hydrogens bonded to heteroatoms in alcohols, phenols, carboxylic acids, amines, amides, and mercaptans were shown to undergo rapid exchange for deuterium during the lifetime of the sample in the CI ion source. Isotope-exchange reactions were also shown to facilitate differentiation of primary, secondary, and tertiary amines when either ND_3[4] or MeOD[5] was used as the CI reagent. Hydrogen–deuterium exchange under GC conditions has been accomplished on column by using either neutral or basic carbowax pretreated with deuterium oxide.[6]

Exchange of aromatic hydrogens in the gas phase was first reported by Beauchamp and co-workers.[7] Using ion cyclotron resonance (ICR) spectroscopy, they observed sequential replacement of hydrogen by deuterium during reaction of protonated benzene ions with D_2O. Several substituted benzene derivatives also incorporated deuterium under ICR conditions but the rate of the isotope exchange reaction showed a strong dependence on the structure of the sample. All four ring hydrogens in the *o*- and *p*-difluorobenzenes exchanged deuterium rapidly whereas only slow incorporation of a single deuterium occurred in the *m*-difluorobenzene isomer. No exchange of aromatic hydrogens was observed in benzene derivatives with strong electron-donating or electron-withdrawing substituents. Many of these compounds protonate on the substituent and it was concluded that ring protonation was a necessary condition for the hydrogen deuterium isotope exchange to occur. Martinson and Buttrill came to the same conclusion on the basis of a CI study of protonated benzene derivatives with D_2O as the reagent gas.[8]

Recently Stewart et al. have shown that $M - 1^-$ ions from esters, olefins, acetylenes, allenes, and toluene undergo hydrogen–deuterium exchange when allowed to react with D_2O under flowing afterglow conditions.[9] In a later paper from the same group, M

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