MINDO/3 calculations, that the nonclassical ion, which should be more charge delocalized, will be probably less well solvated by the nucleophilic solvents commonly used. Since according to the "classical position" the difference between the energies of I and II in solution was small, inclusion of the differential solvation means that this difference in the gas phase should be even smaller. Thus the "classical position"[19] requires that the gas-phase energies of the classical and nonclassical structures should be very close, i.e., both structures lying within an energy plateau. On the other hand, the "nonclassical" position requires that the gas-phase energy of the nonclassical ion is lower (by a small or large amount) than the gas-phase energy of the classical ion. Since the gas-phase energies in Table I showed that the norbornyl cation is endowed with special (~6 kcal/mol) stability, the "classical position" with nearly isoenergetic ions suggests that the same stabilizing factors act on both ions. The significant participation of the C(1)-C(6) bond orbital to the LUMO of the classical norbornyl cation predicted by MINDO/3 (Jorgensen[18]), if real and occurring also in the nonclassical ion, might be such a factor. On the other hand, if reliable future theoretical calculations show that the nonclassical structure is significantly more stable, the special gas-phase stability found experimentally would be explained and the nonclassical position proven correct.

Experimental Section

The measurements were made with a high ion source pressure mass spectrometer used for proton transfer equilibria already described in earlier work.[5,6,20] The techniques used were also the same.[20] The two bases B_1 and B_2 were generally in the 0.5-50-mTorr range and CH_4 was used as a carrier gas at total pressures in the 1-4-Torr range.

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Semiempirical Molecular Orbital Calculation of Atom-Pair Interactions in a Molecule

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Abstract: A simple procedure is proposed to resolve the binding energy calculated from a semiempirical MO method into terms that are representative only of atom-pair interactions. These interactions are comparable to traditional bonded and nonbonded interactions. Practical calculations for a homologous series of compounds require parameter values to be determined for the series. The parameter values may be evaluated unambiguously from key compounds. Examples for the evaluation of parameter values are given for saturated hydrocarbons, amines, alcohols, and ethers using energy quantities obtained from a modified CNDO method. Preliminary calculations are made for benzene, ethylene, and acetylene. Applications of the proposed energy-partitioning technique yield quantum chemical estimates of "bond energies" that are comparable in magnitude to those discussed traditionally.

Introduction

A traditional chemist is interested in the binding energy of a molecule, which is defined as the difference between the total energy of the molecule and the sum of energies of the free atoms that constitute the molecule. On a crude level, the binding energy is simply taken as the sum of average bond energies, representing the interactions between the bonded atoms. To obtain more accurate estimates, the nonbonded

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interactions must also be taken into account. Bond-energy schemes using this approach have proven to be useful in thermochemistry and conformational analysis.[1]

In recent years, calculation of molecular binding energy by the self-consistent-field molecular orbital (SCF MO) method[2] has become a routine practice. Despite many elegant theories of the chemical bond based on quantum mechanics,[3-5] there is still a lack of simple procedures for the resolution of the quantum-chemical binding energy into terms that correspond directly to traditional bonded and nonbonded interactions. The difficulty lies in the fact that an interaction of this type is a concept rather than an observable; hence any attempt to compute such a quantity would necessitate arbitrary assumptions.

The purpose of this work is to suggest a simple procedure to calculate atom-pair interactions based on MOs expanded as linear combinations of atomic orbitals (LCAOs) on various atomic centers. The expression for the binding energy will be partitioned into a sum of two-center energy terms corresponding to these interactions. In view of the objective, a semiempirical MO scheme is the natural method of choice since the three- and four-center energy terms resulting from the expansions have already been eliminated. To illustrate this procedure, the semiempirical SCF MO method with complete neglect of differential overlap (CNDO) of Pople and coworkers[6] will be used.

Development of Procedure

For the CNDO method the total energy of a molecule taking into account only the valence electrons of atoms, E_t, may be expressed as a sum of one-center, E_A, and two-center, E_{AB}, terms as follows:[7]

$$E_t = \sum_{A} E_A + \sum_{A<B}\sum E_{AB} \tag{1}$$

where

$$E_A = \sum_{\mu}^{A} P_{\mu\mu}U_{\mu\mu} + \tfrac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{A} (P_{\mu\mu}P_{\nu\nu} - \tfrac{1}{2}P_{\mu\nu}^2)\gamma_{AA} \tag{2}$$

and

$$E_{AB} = \sum_{\mu}^{A}\sum_{\nu}^{B} (2P_{\mu\nu}\beta_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}^2\gamma_{AB}) + (Z_AZ_BR_{AB}^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}P_{BB}\gamma_{AB}) \tag{3}$$

The indexes μ and ν refer to AOs and A and B to atoms. $P_{\mu\nu}$ is a density matrix element and P_{AA} is the total electron density on A. $U_{\mu\mu}$ describes the one-center core integral and $\beta_{\mu\nu}$ is the core resonance integral. γ_{AA} and γ_{AB} are respectively the one- and two-center electron repulsion integrals, whereas V_{AB} represents the attraction of an electron on atom A by the core of another atom B. $Z_AZ_BR_{AB}^{-1}$ is the nuclear repulsion between core charges Z_A and Z_B separated by an interatomic distance R_{AB}.

The focus of this study is on the binding energy, E_b, which is less than E_t by the sum of the free-atom energies:

$$E_b = E_t - \sum_{A} E_A^0 \tag{4}$$

where E_A^0 is the energy of the valence electrons of free atom A in its ground state. E_A^0 may be expressed in a manner analogous to E_A in eq 2 as

$$E_A^0 = \sum_{\mu}^{A} P_{\mu\mu}^0U_{\mu\mu} + \tfrac{1}{2}\sum_{\mu}^{A} P_{\mu\mu}^0\left(\sum_{\nu}^{A} P_{\nu\nu}^0 - 1\right)\gamma_{AA} \tag{5}$$

with the density matrix elements now referring to the free atom. Substituting eq 1 into eq 4 leads to an expression for E_b in terms of one-center, ΔE_A, and two-center, E_{AB}, terms:

$$E_b = \sum_{A} \Delta E_A + \sum_{A<B}\sum E_{AB} \tag{6}$$

where $\Delta E_A = E_A - E_A^0$. ΔE_A represents the change of energy of atom A in going from a free atom to an atom in a molecule. The objective is to partition E_b into a simple sum of two-center terms, E_{AB}', such that

$$E_b = \sum_{A<B}\sum E_{AB}' \tag{7}$$

The transformation of E_b from a sum of ΔE_A and E_{AB} in eq 6 to simply a sum of E_{AB}' in eq 7 requires the resolution of ΔE_A terms into two-center terms. In the absence of rigorous quantum chemical theories for this resolution, an approximate approach will be followed.

To provide the background for rationalization it would be instructive to use a simple picture to depict the physical processes involved in the formation of a molecule from its constituent atoms. First, imagine the situation when all the atoms A, . . . , N are separated infinitely apart; the energies for the separated atoms would be E_A^0, . . . , E_N^0 and those for the atom pairs, E_{AB}, . . . , E_{MN}, would be zero. Next, imagine the atoms approaching one another along a hypothetical ideal path for the formation of the molecule. Suppose further that a point is chosen along this pathway for examination, which is near the equilibrium geometry but at which the atoms are still sufficiently far enough away from one another so that the energy of atom A is independent of any one- or two-center interaction which does not specifically involve A. As the atoms approach the point, from infinity, the charges on atom A are rearranged owing to bonding and antibonding interactions between A and other atoms B, . . . , N. This charge flow between A and its surroundings has two effects: first it serves to increase the energy of A from E_A^0 to E_A, which gives rise to the ΔE_A term; second, the charge flow gives rise to nonvanishing two-center terms; E_{AB}, . . . , E_{AN}, which are negative or positive depending on a bonding or antibonding situation, respectively. Hence, the rearrangement of charges on A intimately connects ΔE_A and E_{AB}, . . . , E_{AN}. In the operational sense, $\Delta E_A = \Delta E_A(E_{AB}, \ldots, E_{AN})$. This particular functional dependence of ΔE_A will be utilized subsequently for energy partitioning. Finally, consider that the atoms have reached the equilibrium geometry. In this new situation, all atoms are in a closer proximity to A and the interactions among B, . . . , N may now give rise to nonvanishing effects on the energy of A. In other words, ΔE_A is not only a function of E_{AB}, . . . , E_{AN} but also depends upon the terms ΔE_B, . . . , ΔE_N and E_{BC}, . . . E_{MN}. These additional effects are exceedingly difficult to treat mathematically and their explicit inclusion will be omitted.

Based on the above exposition, the resolution of the ΔE_A term proceeds with the following arbitrary assumptions. The change of energy on atom A, ΔE_A, is a simple sum of effects due to the bonding and antibonding interactions between A and every other atom B in the molecule:

$$\Delta E_A = \sum_{B \neq A} \Delta E_A^{(B)} \tag{8}$$

where $\Delta E_A^{(B)}$ is identified as the portion of ΔE_A caused specifically by the interaction of A and B. ΔE_A is dependent on the two-center terms involving A explicitly, E_{AB} ($B \neq A$), but is independent of all one- and two-center terms not involving A, ΔE_B and E_{BC} ($B \neq A$, $C \neq A$). Furthermore, the effect of E_{AB} on ΔE_A is only to the first order. These assumptions may be combined into an equation expressing ΔE_A as a simple additive function of E_{AB} as follows:

$$\Delta E_A = -\tfrac{1}{2} \sum_{B \neq A} W_{AB}E_{AB} \tag{9}$$

where the weighting factor, W_{AB}, is introduced as

$$W_{AB} = -2\Delta E_A^{(B)}/E_{AB} \tag{10}$$

To elucidate the above expressions with an example, take methane, $CH_1H_2H_3H_4$, where the subscripts for H are atom labels. It is reasonable to consider that the increase in energy on C, ΔE_C, may be apportioned as follows:

$$\Delta E_C = \Delta E_C^{(H_1)} + \Delta E_C^{(H_2)} + \Delta E_C^{(H_3)} + \Delta E_C^{(H_4)} \tag{8a}$$

where $\Delta E_C^{(H_1)}$ refers to the portion of ΔE_C attributed to a net charge flow from C to the bonding region between C and H_1. Applying the assumptions embedded in eq 9, ΔE_C is taken to be a function of E_{CH_i}:

$$\Delta E_C = -\tfrac{1}{2}(W_{CH_1}E_{CH_1} + W_{CH_2}E_{CH_2} + W_{CH_3}E_{CH_3} + W_{CH_4}E_{CH_4}) \tag{9a}$$

where E_{CH_1} describes the lowering in energy due to CH_1 bond formation. Hence,

$$W_{CH_1} = -2\Delta E_C^{(H_1)}/E_{CH_1} \tag{10a}$$

Owing to symmetry, $\Delta E_C^{(H_1)} = \Delta E_C/4$, $E_{CH_1} = E_{CH}$, and therefore $W_{CH_1} = W_{CH} = -\Delta E_C/2E_{CH}$.

In a stable molecule for which E_b is negative, ΔE_A is generally positive and E_{AB} is negative for the bonding region. For the nonbonding region, E_{AB} may be either positive or negative and its magnitude is small compared with that of ΔE_A or E_{AB} for the bonding region. Thus W_{AB} for a bonded atom pair AB is expected to be positive considering its relation with ΔE_A and E_{AB} as expressed in eq 9. Conversely, if nonbonded interactions are negligibly small, eq 9 may be interpreted qualitatively as follows: the energy of atom A increases as the total bonding energies associated with atom A decreases.

To allow for symmetry in the summation over two different atoms, it can be shown that

$$\sum_{A} \Delta E_A = \sum_{A<B}\sum -\tfrac{1}{2}(W_{AB} + W_{BA})E_{AB} \tag{11}$$

(Note that E_{BA} is the same as E_{AB}.) Substituting eq 11 into eq 6, the final expression for the binding energy as a simple sum of atom-pair interactions is obtained:

$$E_b = \sum_{A<B}\sum [1 - \tfrac{1}{2}(W_{AB} + W_{BA})]E_{AB} \tag{12}$$

which yields an explicit expression for E_{AB}' in eq 7 as

$$E_{AB}' = [1 - \tfrac{1}{2}(W_{AB} + W_{BA})]E_{AB} \equiv (1 - W_{AB}')E_{AB} \tag{13}$$

The composite weighting factor, W_{AB}', is

$$W_{AB}' \equiv \tfrac{1}{2}(W_{AB} + W_{BA}) = -[(\Delta E_A^{(B)}/E_{AB}) + (\Delta E_B^{(A)}/E_{AB})] \tag{14}$$

Again, in a stable molecule, W_{AB}' for a bonded pair is expected to assume the limits

$$0 < W_{AB}' < 1 \tag{15}$$

so that, if E_{AB} in eq 13 is negative for the bonding region, the corresponding E_{AB}' will also be negative. The combination of eq 13 and 15 leads to the expectation that E_{AB}' for the bonded interactions will have the same sign as E_{AB}, but will assume a smaller magnitude. The physical situation depicted here may be emphasized by considering ΔE_A terms as atom-promotion energies, E_{AB} terms as atom-pair energies, and E_{AB}' terms as net atom-pair energies. (The term "promotion energy" is used descriptively to denote the positive nature of ΔE_A; it is not identical with the conventional definition.)

The net atom-pair energies, E_{AB}', may be compared directly to traditional bonded and nonbonded interactions. The sign and magnitude of E_{AB}' are expected to reflect the nature and strength of interaction between atoms A and B in the atom pair AB. A large negative E_{AB}' implies strong attraction between atoms A and B, while a positive value implies repulsion. Note especially that the binding energy expressed this way is designed to serve a useful and important empirical concept.

The working equations presented thus far may be illustrated by an analysis of methane, CH_4:

$$\begin{aligned} E_b &= \Delta E_C + 4\Delta E_H + 4E_{CH} + 6E_{HCH} \\ &= 4[1 - \tfrac{1}{2}(W_{CH} + W_{HC})]E_{CH} + 6(1 - W_{HH})E_{HCH} \\ &= 4E_{CH}' + 6E_{HCH}' \end{aligned} \tag{16}$$

where the one-center terms are resolved according to the following:

$$\Delta E_C = -2W_{CH}E_{CH} \tag{17}$$

and

$$\Delta E_H = -\tfrac{1}{2}(W_{HC}E_{CH} + 3W_{HH}E_{HCH}) \tag{18}$$

The subscript CH denotes the bonded atom pair C–H, while HCH defines the nonbonded atom pair H···H. Here E_{CH}' represents the 1,2 CH bonded interaction and E_{HCH}' corresponds to the 1,3 HCH nonbonded interactions.

To calculate E_{AB}' according to eq 13, the numerical values of W_{AB} and W_{BA} must be known. In the derivation, W_{AB} is related to the ratio between $\Delta E_A^{(B)}$ and E_{AB} as shown in eq 10. A moment's reflection reveals that $\Delta E_A^{(B)}$ term is a theoretical construct for conveying a necessary idea and is not directly derivable from the expressions given for E_A and E_A^0 in eq 2 and 5. Therefore W_{AB} cannot be calculated directly from basic charge density terms and AO integrals. The alternative is to treat the W_{AB} as parameters and find reasonable values for them from the available values of ΔE_A and E_{AB} from some key compounds via eq 9.

Evaluation of Parameter Values

A systematic procedure for calculating the W_{AB} of bonded atom pairs for a given homologous series of compounds begins with a consideration of the few compounds for which unambiguous assignment of W_{AB} may be made. Taking the saturated hydrocarbons as an example, W_{HH} is determined uniquely from the hydrogen molecule, H_2, because of symmetry, and, similarly, W_{CH} from CH_4. Given the assigned value of W_{CH} derived from CH_4, W_{CC} can be calculated from ethane, CH_3CH_3. Labeling parameter values obtained from the key compounds as W_{AB}^0, the suggested procedure for the derivation of W_{HH}^0, W_{CH}^0, W_{HC}^0, and W_{CC}^0 is illustrated below:

$$H_2\!: \quad W_{HH} = -2\Delta E_H/E_{HH} \equiv W_{HH}^0 \tag{19}$$

$$CH_4\!: \quad W_{CH} = -\Delta E_C/2E_{CH} \equiv W_{CH}^0 \tag{20}$$

$$W_{HC} = -(2\Delta E_H + 3W_{HH}^0E_{HCH})/E_{CH} \equiv W_{HC}^0 \tag{21}$$

$$CH_3CH_3\!: \quad W_{CC} = -[2\Delta E_C + 3W_{CH}^0(E_{CH} + E_{CCH})]/E_{CC} \equiv W_{CC}^0 \tag{22}$$

Central to this procedure is the assumption that the W_{AB}^0 fitted from bonded pairs are applicable to the nonbonded pairs; e.g., W_{HH}^0 determined from the HH bonded interaction in H_2 of eq 19 is used for the HCH nonbonded interactions in CH_4 of eq 21. The assumption is clearly difficult to justify but is tolerated for the present in order to retain a simple procedure.[7] Considering the fact that the magnitude of E_{AB} of a nonbonded interaction is relatively negligible, this impropriety in the usage of W_{AB} for the nonbonded pairs is not expected to affect the overall calculations in any decisive manner.

Recognizing that the W_{AB}^0 fitted from some key compounds need not be identical with the W_{AB} in the compound of interest, and that ΔE_A must be fully resolved into two-center terms as prescribed by eq 9, a normalizing factor, N_A, is introduced to

Table I. MCNDO Binding Energies for Key Compounds (kcal/mol)[a]

compd	$\Delta H°_f$(exptl)[b]	E_b(MCNDO)[a]	deviation[c]
H_2	0.00	−104.31	−0.11
CH_4	−17.89	−397.10	0.09
NH_3	−10.97	−280.10	0.17
H_2O	−57.80	−221.41	0.15
CH_3CH_3	−20.24	−677.37	−2.73
CH_3NH_2	−5.50	−550.34	−0.44
CH_3OH	−48.07	−487.94	−1.01

[a] See ref 8 for details of MCNDO calculations. Note that tetrahedral bond angles are used uniformly for the chosen compounds. The free atom energies $E_A{}^0$ based on valence electrons for the atoms H, C, N, and O are −0.5, −5.754 96, −10.418 44, and −17.107 53 au, respectively. [b] Heat of formation in the gas phase at 25 °C. Data are taken from "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1971). [c] Deviation = E_b(MCNDO) − E_b(exptl). E_b(exptl) is calculated from $\Delta H°_f$(exptl) using $\Delta H°_f$ for the atoms H, C, N, and O as 52.1, 170.9, 113.0, and 59.69 kcal/mol, respectively.

Table II. Model Calculations with MCNDO Values for H_2

term	eq	expression and value
ΔE_H	2, 6	$\Delta E_A = {}^1\!/_4\gamma_{AA} = 113.73$ kcal/mol
E_{HH}	3	$E_{AB} = 2\beta_{AB} - {}^1\!/_2\gamma_{AB} + (R_{AB}{}^{-1} - 2V_{AB} + \gamma_{AB} = -331.78$ kcal/mol
W_{HH}	9, 19	$W_{AB} = -2\Delta E_A/E_{AB} = 0.6856$
E_{HH}'	13	$W_{AB} = W_{BA} = W_{AB}'$ in this case $E_{AB}' = (1 - W_{AB}')E_{AB} = -104.31$ kcal/mol

compensate for small environmental differences encountered in going from one compound to another in the same series:

$$\Delta E_A = -{}^1\!/_2 N_A \sum_{B \neq A} W_{AB}{}^0 E_{AB} \tag{23}$$

N_A can be calculated directly from the defining equation as

$$N_A = -2\Delta E_A / \sum_{B \neq A} W_{AB}{}^0 E_{AB} \tag{24}$$

Matching eq 23 against eq 9 reveals a linear relationship between W_{AB} and $W_{AB}{}^0$:

$$W_{AB} = N_A W_{AB}{}^0 \tag{25}$$

Again, it may be of interest to speculate on the values of N_A based on the physical meanings of eq 23 and 25. N_A will be exactly unity in a key compound if $W_{AB} = W_{AB}{}^0$ for all B. Ordinarily, N_A gives a measure of the deviation of the energetic state of atom A in the compound being considered from the corresponding state of atom A in the key compound. If both compounds belong to the same homologous series, N_A is expected to be very close to unity, since the two states of atom A should be fairly similar. This expectation is built upon the empirical evidence that compounds in the same series have very similar chemical properties. If $N_A \simeq 1$, then $W_{AB} \simeq W_{AB}{}^0$ for all B and the inherent error in eq 23 for using a single factor N_A instead of multiple factors N_{AB} is minimized.

To exemplify the calculation of N_A, the key compounds H_2, CH_4, and CH_3CH_3 are again used. With respect to eq 19–22 for the derivations of the specific $W_{AB}{}^0$, the factors N_H in H_2, N_C and N_H in CH_4, and N_C in CH_3CH_3 have the value of unity automatically. But for the H atoms in CH_3CH_3, N_H must be determined separately:

$$CH_3CH_3\colon N_H = -2\Delta E_H/[W_{HC}{}^0 E_{CH} + W_{HH}{}^0(2E_{HCH} + E^A{}_{HCCH} + 2E^G{}_{HCCH})] \tag{26}$$

where the superscripts A and G denote the repective anti and gauche conformations of the 1,4 HCCH interactions. W_{HH} and W_{HC} in CH_3CH_3 are next determined as

Table III. Calculations with MCNDO Values for XH_m[a]

term	type[b]	CH_4	NH_3	H_2O
ΔE_A	X	544.66	504.17	404.87
	H	117.49	122.49	129.63
E_{AB}	XH	−358.81	−391.94	−450.39
	HXH	3.91	8.03	15.23
W_{AB}	XH	0.7590	0.8576	0.8989
	HX	0.6773	0.6531	0.5988
E_{AB}'	XH	−101.13	−95.89	−113.10
	HXH	1.23	2.52	4.79

[a] All energy terms are in kcal/mol. X represents C, N, or O, [b] For a nonbonded atom pair AB, the two terminal atoms A···B in AXB, AXYB, AXYZB, and AWXYZB are those involved in the pair.

$$W_{HH} = N_H W_{HH}{}^0 \text{ and } W_{HC} = N_H W_{HC}{}^0 \tag{27}$$

Results of MCNDO Calculations

To find out how practical the proposed procedure is with regard to the calculation of bonded and nonbonded interactions, a modified CNDO (MCNDO) method developed recently[8] to yield good binding energies for certain saturated hydrocarbons, amines, alcohols, and ethers is used for the analysis. For the three homologous series being considered, it is necessary to examine seven key compounds in order to evaluate all required parameter values for $W_{AB}{}^0$; hydrogen, methane, ammonia, water, ethane, methylamine, and methanol. Table I lists the MCNDO binding energies of the key compounds and their deviations from experimental values based on heats of formation, $\Delta H°_f$, at 25 °C. Table II demonstrates the various computational steps involved in this procedure, using the simplest compound, H_2, as an example. Tables III and IV provide MCNDO values for the remaining six key compounds, XH_m and CH_3XH_n, where X represents C, N, or O. Table V summarizes the values of $W_{AB}{}^0$ thus obtained from all seven key compounds.

As an initial test of the usefulness of the procedure, E_{AB} and E_{AB}' for certain bonded interactions in CH_3XH_n are compared with Pauling's thermochemical bond energies[9] in Table VI. It is to be noted that bond energies are calculated without taking into account the nonbonded interactions. Comparisons of E_{AB} and E_{AB}' with bond energies would be appropriate only if the nonbonded interactions are negligible. The MCNDO values for the nonbonded interactions shown in Table IV are indeed two orders of magnitude smaller than those for the bonded interactions.[10] Under the circumstances, such comparisons are assumed acceptable.

The bond energy values listed in Table VI indicate the following trends for the bonded interactions:

$$E(\text{C–O}) > E(\text{C–C}) > E(\text{C–N}) \tag{a}$$

$$E(\text{O–H}) > E(\text{C–H}) > E(\text{N–H}) \tag{b}$$

$$E(\text{O–H}) > E(\text{C–O}),\ E(\text{C–H}) > E(\text{C–C}),\ \text{and } E(\text{N–H}) > E(\text{C–N}) \tag{c}$$

where E(A–B) denotes the bond energy of a single bond between atoms A and B. (The sign adoption in thermochemistry is positive for attraction, exactly opposite to that employed in quantum mechanics. Thus E(A–B) must be compared with $-E_{AB}$ or $-E_{AB}'$.)

The MCNDO values for the net atom-pair energies, E_{AB}', support all the above trends except for a reversal of order for the C–O and C–C interactions in (a); i.e.

$$-E_{C\text{-}C}' > -E_{C\text{-}O}' > -E_{C\text{-}N}' \tag{a'}$$

where the form of the subscript for E_{AB}' is adopted to facilitate

Table IV. Calculations with MCNDO Values for CH_3XH_n[a]

term	type[b]	CH_3CH_3	CH_3NH_2	CH_3OH
ΔE_A	C	549.69	550.33	553.34
	X		503.56	399.31
	H	116.33	115.92; 115.14[c]	115.15; 116.28
	H*		121.97	130.15
E_{AB}	CX	−386.81	−395.08	−439.61
	CH	−355.75	−356.46; −356.62	−356.69; −356.19
	XH		−388.29	−445.56
	CXH	3.05	5.01	9.61
	XCH		3.92; 3.57	3.98; 4.11
	HCH	4.28	4.57; 4.47	4.67 4.70
	HXH		8.60	
	HCXH anti	−0.94	−0.86	−0.59
	gauche	0.90	1.12; 0.94	1.13
W_{AB}	CX	0.7660	0.7505	0.6874
	XC		0.8883	0.9302
N_A	H	1.0011	0.9972; 0.9941	0.9926; 0.9991
	H*		1.0019	1.0045
E_{AB}'	CX	−90.52	−71.36	−84.05
	CH	−100.14	−100.81; −101.23	−101.42; −100.50
	XH		−94.76	−111.29
	CXH	0.86	1.41	2.69
	XCH		0.96; 0.88	1.01; 1.03
	HCH	1.34	1.45; 1.41	1.48; 1.50
	HXH		2.69	
	HCXH anti	−0.29	−0.27	−0.18
	gauche	0.28	0.35; 0.30	0.35

[a] See footnotes *a* and *b*, Table III. [b] For ΔE_A and N_A, H and H* denote H atoms bonded to C and X, respectively. [c] In the methyl group of CH_3NH_2 or CH_3OH, there are two symmetry-equivalent H atoms and one symmetry-unique H atom. The value that occurs twice due to the H atom in the equivalent group is presented first.

recognition of bonding arrangements. The reversal could be due to an overestimation of the C–C interaction by the MCNDO method.[10] With regard to magnitudes, the E_{AB}' are consistently more attractive, which is to be expected since the generally repulsive nonbonded interactions have not been included prior to the comparisons. As to the degree of agreement, the $-E_{AB}'$, with the exception of $-E_{C\text{-}C}'$, fall within the relatively narrow range of 0–2 kcal/mol above Pauling's values. This close agreement is indeed surprising.

The MCNDO values for the atom-pair energies, E_{AB}, on the other hand, give the following trends for the bonded interactions:

$$-E_{C\text{-}O} > -E_{C\text{-}N} > -E_{C\text{-}C} \qquad (a'')$$

$$-E_{O\text{-}H} > -E_{N\text{-}H} > -E_{C\text{-}H} \qquad (b'')$$

$$-E_{O\text{-}H} > -E_{C\text{-}O},\ -E_{C\text{-}N} > -E_{N\text{-}H}, \text{ and } -E_{C\text{-}C} > -E_{C\text{-}H} \qquad (c'')$$

Item by item comparisons with the bond energy trends reveal four contradictions in the relative magnitudes of interactions: C–N vs. C–C, N–H vs. C–H, C–N vs. N–H, and C–C vs. C–H. Such anomalies need not mean failure, since the E_{AB} have, in many instances, been found to be truer measures of the intrinsic bond strengths than are bond energies if criteria such as equilibrium interatomic distances and force constants are used.[4] Yet the extraordinarily large magnitudes of E_{AB} are somewhat disconcerting to chemists. For example, an energy value such as 356 kcal/mol (from $-E_{C\text{-}H}$) for a C–H bond surely sounds less familiar than the value 100 kcal/mol (from $-E_{C\text{-}H}'$).

Table V. MCNDO Values of W_{AB}^0 [a]

atom A	atom B H	C	N	O
H	0.6856	0.6773	0.6531	0.5988
C	0.7590	0.7660	0.7505	0.6874
N	0.8576	0.8883		
O	0.8989	0.9302		

[a] Compiled from W_{AB} values in Tables II, III, and IV.

Table VI. Comparison of Calculated Bonded Interactions in CH_3XH_n and Thermochemical Bond Energies (kcal/mol)[a]

type	$-E_{AB}$	$-E_{AB}'$	Pauling
C–C	386.81	90.52	82.2
C–N	395.08	71.36	69.8
C–O	439.61	84.05	83.7
C–H	355.75	100.14	99.2
N–H	388.29	94.76	93.5
O–H	445.56	111.26	110.7

[a] See Table IV and ref 9.

In the observation just made lies the very reason for proposing this new procedure for energy partitioning. The new E_{AB}' terms for the bonded interactions actually may be thought to represent the kind of bond energy terms which have been taught to the students of chemistry during the past 3 decades.[9] The fact that the concept of bond energy has survived the test of time proves the practical significance of the idea, regardless of how arbitrary the concept may be in the final analysis.

In the proposed procedure, the introduction of the weighting factor W_{AB} plays the key role in the systematic dissection of ΔE_A terms for mergers with E_{AB} terms to form E_{AB}' terms. W_{AB} is calculated via the parameter W_{AB}^0, derived basically for the bonded pairs in certain key compounds, and the normalizing factor N_A, which gives a measure of the deviation of W_{AB} from W_{AB}^0. Results for W_{AB}^0 listed in Table V show uniformly positive numbers, in agreement with the deduction from the earlier analysis. In addition, W_{AB}^0 values confirm the expected limits:

$$0 < \tfrac{1}{2}(W_{AB}^0 + W_{BA}^0) < 1$$

To examine values of N_A, species other than the key compounds must be used. For this study 12 hydrocarbons, 10 amines, and 12 alcohols and ethers were selected; all these compounds were treated previously by the MCNDO method.[8] Results for N_A pertinent to this discussion are presented in Tables VII and VIII. A more complete presentation of results of energy partitioning in these compounds will be given elsewhere.[10]

Atoms of the same atomic number in compounds of the same series are involved in the same types of bonding, but may encounter different kinds of bonding environment. For the chosen compounds, the distinct atoms are H, C, N, and O; all are engaged in single bonds. The bonding environment may be roughly described by the terms primary, secondary, tertiary, or quaternary for C, primary, secondary, or tertiary for N, and primary or secondary for O. The bonding environment for H may be described by the kind of atom to which it is bonded. To facilitate discussion, atoms of the same atomic number which experience the same kind of bonding environment are called the same kind of atoms. For example, a primary C atom is taken to be a different kind of C atom than a quaternary C

Table VII. MCNDO Values of N_A in Saturated Hydrocarbons, Amines, Alcohols, and Ethers[a]

A. Compounds Used

hydrocarbons:	propane, *n*-butane, 2-methylpropane, *n*-pentane, 2-methylbutane, 2,2-dimethylpropane
amines:	ethylamine, dimethylamine, *n*-propylamine, isopropylamine, trimethylamine, *n*-butylamine, isobutylamine, *sec*-butylamine, *tert*-butylamine, diethylamine
alcohols and ethers:	ethanol, dimethyl ether, 1-propanol, 2-propanol, methyl ethyl ether, 1-butanol, 2-methyl-1-propanol, 2-butanol, 2-methyl-2-propanol, diethyl ether, methyl *n*-propyl ether, methyl isopropyl ether

B. Average Values of N_A[b]

series	atoms[c]	kind[d]	$\bar{N}_A$	S
hydrocarbons	C	primary	1.0008	0.0004
		secondary	0.9995	0.0002
		tertiary	0.9976	0.0002
		quaternary	0.9938	
	H	primary C	1.0031	0.0010
		secondary C	1.0046	0.0008
		tertiary C	1.0057	0.0012
amines	N	primary	1.0018	0.0010
		secondary	0.9990	0.0012
		tertiary	0.9926	
	H*	primary N	1.0019	0.0005
		secondary N	1.0055	0.0015
alcohols and ethers	O	primary	1.0022	0.0013
		secondary	0.9984	0.0009
	H*	primary O	1.0019	0.0002

[a] The MCNDO energy terms resulting from ref 8 and $W_{AB}{}^0$ values of Table V are used for the analysis. [b] The average value $\bar{N}_A$ and the standard deviation S for a given kind of atom A in the series are calculated as follows: $\bar{N}_A = (\Sigma_i f_{A,i} N_{A,i})/f_A$ and $S = [f_{A,i} N_{A,i}{}^2 - f_A{}^2 \bar{N}_A]/(f_A - 1)^{1/2}$, where $f_{A,i}$ and $N_{A,i}$ represent the number and average value for A in compound i and $f_A = \Sigma_i f_{A,i}$. [c] H and H* denote H atoms bonded to C and to N or O, respectively. [d] Describes the kind of C, N, or O atom either directly or as the atom bonded to H or H*.

Table VIII. MCNDO Values of N_A in Saturated Cyclic Hydrocarbons[a,b]

	C atom		H atom	
compd	secondary	tertiary	secondary	tertiary
cyclopropane	1.0187		0.9925	
cyclobutane	1.0131		0.9994	
cyclohexane	1.0002		1.0036	
trans-decalin	1.0007	0.9989	1.0051	1.0108
cis-decalin	1.0012	0.9991	1.0055	1.0085
adamantane	1.0012	0.9995	1.0068	1.0064

[a] See footnotes *a*, *c*, and *d*, Table VII. [b] Average values of N_A are used in cases where the atoms involved are not symmetry equivalent.

atom. For each kind of atom A occurring in the same saturated acyclic series, the average value of N_A, $\bar{N}_A$, as well as its standard deviation, S, is presented in Table VII. Values of N_A for selected saturated cyclic hydrocarbons, classified in the same manner, are shown in Table VIII.

Values of $\bar{N}_A$ in Table VII range from 0.9926 to 1.0057, which is within 0.8% of unity. The closeness of N_A values to unity supports the earlier speculation that $W_{AB} \simeq W_{AB}{}^0$ for all B when the compounds under consideration are in the same series as the key compounds. Now consider the more exacting classification of atoms into kinds. Different kinds of atoms do indeed have slightly different $\bar{N}_A$. For each kind of atom, $\bar{N}_A$ has a standard deviation of no more than 0.15%. The near constancy of N_A values for the same kind of atoms suggests that the classification is meaningful. The empirical evidence that C-H bonds in alkanes vary slightly in length according to the kind of C atoms involved also lends credence to the classification. In propane and 2-methylpropane, for example, the C-H bond lengths are respectively 1.091, 1.096, and 1.108 Å for the primary, secondary, and tertiary C atoms involved.[11]

The cyclic alkanes differ structurally from their acyclic counterparts by having closed-ring rather than open-chain carbon skeletons. This difference in the C-C bond disposition manifest itself in the different N_C values for secondary and tertiary C atoms: those listed in Table VIII for the cyclic species are uniformly larger than those for the corresponding acyclic compounds in Table VII. More interesting is the observation that the N_C for cyclopropane and cyclobutane are between 1 and 2% greater than unity; these are significant deviations, considering a maximum deviation of only 0.8% encountered from the acyclics. Compounds containing cyclohexane rings, on the other hand, have N_C values close to unity. These numerical values are consistent with the knowledge that small ring compounds have large "ring strain" energies relative to their "strainless" open-chain counterparts. The strain arises from substantial distortion of the CCC bond angles in the small rings as compared with the tetrahedral bond angle attributed to C atoms with sp^3 hybridization. Using this argument, the cyclohexanoids would have much less ring strain.

Results of energy partitioning obtained thus far are definitely in good agreement with chemical knowledge. The next question is whether the procedure is applicable to systems other than saturated ones. Unfortunately, MCNDO wave functions for systems other than the ones mentioned already are lacking at the present. In view of the immediate interest in this study, a short-cut approach was chosen to generate MCNDO wave functions for benzene, ethylene, and acetylene. Details and results of calculations are summarized in Table IX. Since the MCNDO parametrization in this case is rather primitive, the calculations must be considered preliminary.

In carrying out the energy-partitioning steps, the effects incurred as a result of different hybridizations on the C atoms must be taken into account. Chemically, the change of hybridization on the C atoms from sp^3 in ethane to sp^2 in benzene and ethylene and to sp in acetylene affects the strengths of the bonds involving the C atoms. In the current context, both W_{CC} and W_{CH} will be affected. According to eq 10, the pertinent factors are defined as

$$W_{CC} = -2\Delta E_C{}^{(C)}/E_{CC} \text{ and } W_{CH} = -2\Delta E_C{}^{(H)}/E_{CH}$$

These expressions reveal that the change in hybridization must affect W_{CC} more drastically than W_{CH}, since the $\Delta E_C{}^{(C)}$ and E_{CC} terms now concern different CC bond types, including the C—C, C=C, C≡C, and the benzenoid $C_b \dot{-} C_b$ bonds. W_{CH} should also change, but only slightly, as $\Delta E_C{}^{(H)}$ and E_{CH} still deal with only one bond type, C-H. However, owing to the increasing s character in going from sp^3 to sp^2 and to sp, the C-H bond strength is expected to increase slightly. Empirically, this subtle change in the C-H bond character is partially reflected through a decrease in the C-H bond lengths in going from ethane to ethylene and to acetylene (1.091, 1.086, and 1.060 Å, respectively).[12]

In order to simplify calculations, a compromise is made to improve the W_{CC} values but not the W_{CH} values, as the change in W_{CH} is expected to be relatively small. Using these newly determined values of W_{CC} from Table IX, the resulting $E_{AB}{}'$ are compared with Laidler's bond-energy values[13] in Table X. The Laidler scheme, being one of the modern bond-energy schemes, attempts to differentiate the characters of different types of C-H bonds. According to Laidler, the following trends

Table IX. Preliminary MCNDO Calculations with Benzene, Ethylene, and Acetylene[a]

		benzene	ethylene	acetylene
		Bond Distances (Å)		
R_{CC}		1.40	1.34	1.20
R_{CH}		1.08	1.08	1.06
		New Parameters for β_{CC}		
K_{CC}		0.9320	0.9482	0.9518
		Energy Terms (kcal/mol)[b]		
E_b		−1318.34	−537.74	−391.67
ΔE_A	C	549.01	541.03	531.00
	H	116.27	117.60	122.82
E_{AB}	CC	−545.16	−681.49	−966.78
	CH	−357.94	−361.16	−374.98
	CCC	5.67		
	CCH	6.73	5.68	8.70
	HCH		6.08	
	CCCC	0.00		
	CCCH	−1.19		
	HCCH	1.38	cis 1.82 trans −1.31	0.00
	CCCCH	−0.14		
	HCCCH	0.07		
	HCCCCH	0.05		
		Energy Partition[c]		
W_{CC}		0.7736	0.7960	0.8109
N_H		0.9980	0.9956	0.9902

[a] The standard geometrical model described in ref 6 is used. Except for the parameter K_{CC}, all other parameters follow those in ref 8. [b] See footnote *b*, Table III. [c] Using W_{HH}^0, W_{CH}^0, and W_{HC}^0 in Table X but reparametrizing W_{CC}^0.

Table X. Comparison of Calculated Bonded Interactions in Hydrocarbons and Thermochemical Bond Energies (kcal/mol)[a]

type	compd	$-E_{AB}'$	Laidler
C—C	ethane	90.52	85.48
$C_b\dot{-}C_b$	benzene	123.42	119.17
C=C	ethylene	139.02	133.00
C≡C	acetylene	182.82	183.28
C—H	ethane	100.14	98.19
	benzene	101.14	100.53
	ethylene	103.33	101.19
	acetylene	106.93	104.19

[a] See Tables VI and IX and ref 13.

are observed:

$$E(\mathrm{C{\equiv}C}) > E(\mathrm{C{=}C}) > E(\mathrm{C_b\dot{-}C_b}) > E(\mathrm{C{-}C}) \quad \text{(d)}$$

$$E(\text{C-H})\text{: acetylene} > \text{ethylene} > \text{benzene} > \text{ethane} \quad \text{(e)}$$

It is gratifying to find that the E_{AB}' from energy partitioning are in exact agreement with these trends. In particular, the simple improvement given to W_{CC} is found to be sufficient to induce the proper trend for the strengths of the different C-H bonds.

From the above calculations the new W_{CC} for the chosen unsaturated compounds may be regarded as the parameter W_{CC}^0 for the new hydrocarbon series of benzenoids, alkenes, and alkynes, as benzene, ethylene, and acetylene may well serve as key compounds for their respective series. To differentiate the various W_{CC}^0, the state of the "first" C atom of the atom pair CC as well as the type of the CC bond should be taken into consideration. For example, the W_{CC} values listed in Tables IV and IX may be relabeled as follows:

$$W(\mathrm{C_{sp^3}{-}C})^0 = 0.7660,\ W(\mathrm{C_b\dot{-}C})^0 = 0.7736,$$
$$W(\mathrm{C_{sp^2}{=}C})^0 = 0.7960, \text{ and } W(\mathrm{C_{sp}{\equiv}C})^0 = 0.8109$$

Similarly, four corresponding W_{CH}^0 are expected:

$$W(\mathrm{C_{sp^3}\text{-}H})^0,\ W(\mathrm{C_b\text{-}H})^0,\ W(\mathrm{C_{sp^2}\text{-}H})^0, \text{ and } W(\mathrm{C_{sp}\text{-}H})^0$$

although the value of $W(\mathrm{C_{sp^3}\text{-}H})^0 = 0.7590$ is also used to represent the other three W_{CH}^0 in the present calculations for computational expediency.

The purpose of working through the unsaturated compounds is to demonstrate that W_{AB}^0 for a given bonded atom pair AB may assume different values depending on the state of atom A and the type of AB bond, both of which are influenced by hybridization, penetration sharing, delocalization, charge transfer, etc.[4,5] To obtain chemically meaningful results, it is mandatory that one assures a proper matching between the bonding characteristics expressed in W_{AB} for the compound concerned and those in W_{AB}^0 of the key compound. A test for the compatibility of the W_{AB}^0 is automatically provided for by the calculation of N_A. If the deviation of N_A from unity is substantial (e.g., greater than 0.8%), a new W_{AB}^0 deduced from a more suitable choice of key compound will be required. In the rare case where AB represents a bond of less definitive nature and no suitable key compound is found, one may alway begin with a trial value (some chemically meaningful value) for W_{AB}^0 and then adjust the value systematically until the resulting N_A appears to be close to unity.

Upon reviewing the W_{AB}^0 and N_A values obtained from the calculations, it is clearly evident that their variations could be both interesting and significant. Notice the regularity in trends evidenced by the W_{AB}^0 values in Table V and the N_A values in Tables VII and VIII for the saturated systems. Typical examples include the more drastic changes of W_{AB} involving atoms of increasing electronegativities:

$$W_{HH} > W_{HC} > W_{HN} > W_{HO}$$
$$\text{and } W_{HH} < W_{CH} < W_{NH} < W_{OH}$$

and the finer variations of W_{CC} among saturated hydrocarbons reflected by the N_C terms:

$$N_C \text{ (primary)} > N_C \text{ (secondary)}$$
$$> N_C \text{ (tertiary)} > N_C \text{ (quaternary)}$$

or

$$W(\mathrm{C_p\text{-}C}) > W(\mathrm{C_s\text{-}C}) > W(\mathrm{C_t\text{-}C}) > W(\mathrm{C_q\text{-}C})$$

where p, s, t, and q differentiate the bonding environments of the first C atom. Note further that after the transition is made to the unsaturated hydrocarbons, an additional trend is given by W_{CC} in Table IX.

$$W(\mathrm{C_{sp^3}{-}C}) < W(\mathrm{C_b\dot{-}C}) < W(\mathrm{C_{sp^2}{=}C}) < W(\mathrm{C_{sp}{\equiv}C})$$

All these trends carry chemical meanings; the problem is to understand their ramifications. It is plausible that the calculated W_{AB}^0 and N_A, or simply the related $\Delta E_A^{(B)}$, terms may serve as chemically meaningful indexes, in addition to the E_A and E_{AB} terms being employed currently.[6,14a]

As regards future development of the procedure, some comments may be made. With respect to theory, a better understanding of the interrelationships between the ΔE_A and E_{AB} terms is needed for setting limits of reliability on the assumptions built in eq 8, 9, and 10. For practical calculations, flexibility should be exercised in the determination of the parameter values. The method of finding W_{AB}^0 values described in this work has been designed specifically to illustrate the logic of approach by simple algebraic relations. It could be either elaborated upon for better numerical accuracies or simplified for adoption in more complex molecular systems. For example, more suitable values for W_{AB}^0 may be achieved by averaging the W_{AB} values derived from a number of representative compounds rather than the few limited key compounds of high symmetry. In systems containing several sufficiently different bond types, the $W_{AB}{}^0$ for nonbonded pairs need be set to zero arbitrarily for reducing the number of parameters.[7]

To summarize, theoretical concepts leading to a simple procedure of partitioning the binding energy into atom-pair interactions are sketched. Preliminary applications of the procedure to saturated systems, complemented by the use of MCNDO wave functions, have given results in good agreement with thermochemical bond energies and existing chemical evidences. Though lacking in theoretical rigor, the procedure has been amply justified in both credibility and utility by its empirical success.

Comparison with Other Methods

Quantum mechanical methods for the study of chemical bonds and calculation of related energy quantities have been developed along several directions.[4,5,14-16] The approach most favored by quantum chemists appears to be the "localized MO" model proposed by Ruedenberg[5] and others.[17,18] The method employs some physical criterion for the derivation of localized MOs from the delocalized canonical MOs[2] by means of an orthogonal transformation. The assets of the method are obviously tied to the conceptual clarity and mathematical rigor with which the model is formulated, but the numerical involvement for its execution is generally extensive, especially for large molecules.

Within the confines of the canonical MOs, a natural partitioning of the total energy into contributions from one-, two-, three-, and four-center terms is feasible. This inherited feature of the LCAO model was utilized by Clementi and co-workers for the study of the stabilities of simple polyatomics.[19] By means of the CNDO approximation, Pople and co-workers eliminated the three- and four-center terms and derived particularly simple expressions for the one- and two-center terms.[6] These terms have been used for correlations with experimental data, especially for organic molecules.[14,20]

In this work the energy-partitioning technique of Pople is being extended. The new method aims at the elimination of the one-center terms in the binding energy so as to obtain net two-center terms. It can be easily adapted to the existing semiempirical MO methods such as extended Hückel, CNDO, INDO, NDDO, and MINDO.[21,6,22] The necessary requirement is to evaluate the set of parameter values appropriate to the method in use. In view of the widespread use of these MO computer programs[23] and the general interest in conformational analysis among chemists, the implementation of the new technique may prove to be a simple and useful matter.[10]

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