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On CNDO Bond Indices and Relations to Molecular Energies*

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An empirical bond strength index is proposed which makes use of the CNDO orbital bond orders in a way appropriate for molecular summation. The index properly summed over all bonds is shown capable of precisely correlating the stabilities of a variety of hydrocarbons as reflected by their heats of formation. Analysis of the form of the relationship between the heats and indices, and comparisons with a similar correlation of stabilities with total binding energies as computed by the CNDO method, reveals the bond indices as precise measures of the two-center molecular energies. Exchange contributions which are dependent upon the square of bond-order terms, electron-nuclear attractions and electron-electron and nuclear-nuclear repulsions are shown to quite precisely cancel each other as contributions to the heats. Effects of structure (ring *vs.* chain configuration) and hybridization are analyzed with respect to their contributions to the binding energies and hence to the heats of formation.

Ein empirischer Index für Bindungsstärken auf Grund von Bindungsordnungen von CNDO-Funktionen wird vorgeschlagen. Er gibt die Stabilitäten von Kohlenwasserstoffen genau wieder. Die Analyse zeigt, daß die Bindungsindizes ein Maß für die molekularen Zweizentrenenergien sind. Die Beiträge auf Grund von Austausch, die von der Bindungsordnung quadratisch abhängen, Elektronen-Kern-Anziehung und Elektronen-Elektronen- sowie Kern-Kern-Abstoßung heben sich in bezug auf die Bildungswärme nahezu heraus. Der Einfluß der Struktur und der Hybridisierung wird ebenfalls im Hinblick auf Bindungs- und Bildungsenergie untersucht.

Un indice empirique de force de liaison est obtenu en utilisant les indices de liaison des orbitales CNDO d'une manière appropriée à la sommation moléculaire. Cet indice convenablement sommé sur toutes les liaisons s'avère fournir une corrélation précise avec la stabilité d'une série d'hydrocarbures mesurée par leur chaleur de formation. L'analyse de la forme de cette relation entre indice et chaleur de formation, ainsi que la comparaison avec une corrélation similaire entre la stabilité et l'énergie de liaison totale calculée par la méthode CNDO, montre que cet indice est une mesure précise de l'énergie moléculaire bicentrique. Les contributions d'échange qui dépendent du carré des indices de liaison, les attractions nucléaires et les répulsions électron-électron, noyau-noyau se compensent exactement dans leur contribution aux chaleurs de formation. Les effets de structure (configuration en cycle ou en chaîne) et l'hybridation sont analysés dans leurs contributions aux énergies de liaison et aux chaleurs de formation.

Introduction

The approximate self-consistent molecular orbital method (versions CNDO/1 and /2) introduced by Pople, Santry and Segal [1] and such improvements as INDO [2] have been shown to significantly aid in the understanding of bonding in molecules of moderate complexity [3]. Besides the various energy contributions of the valence electrons and nuclei of the molecule, the method provides the charge density-bond order matrix, P, upon which the SCF procedure directly

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depends. (The charge densities which are the diagonal matrix terms, and the bond orders, where $\mu \neq \nu$, are defined with neglect of overlap by $P_{\mu\nu} = \sum_i^{\text{occ}} n_i C_{i\mu} C_{i\nu}$, where the i-th MO function, $\psi_i = \sum C_{i\mu} \phi_\mu$, runs over all AO, μ.)

In a desire to correlate molecular stabilities and, thereby, reactivities with quantities derivable from CNDO/2 wave functions for which Mulliken overlap population analysis [4] is not suited because of overlap neglect, the localized "bond index", $\sum P_{\mu\nu}^2$, between any two atoms, was introduced as a measure of bond character [5], and thereafter employed in MO as well as valence bond studies [6]. The apparent virtues of this index are that rotational invariance in the sums of orbital terms between atom pairs is guaranteed, and that a simple sum rule for all (including intraatomic) interactions of a given atom pertains. Bond orders for all (including intraatomic) interactions of a given atom pertains. Bond orders for all orbital pairs or, for that matter, for all atom pairs, are not all positive, however. Negative values imply antibonding interactions, a distinction which is lost upon adoption of the squaring procedure.

We here suggest a new index of bond strength which avoids the above difficulty and demonstrate its potentially broad utility by consideration of how it correlates the bonding properties of a variety of hydrocarbons. Further analysis is carried out to show how the present index is simply relatable to the total molecular energy calculated by the CNDO/2 method and how, therefore, correlations of heats of formation by the total energies [7] may be interpreted with enhanced understanding through the bond orders.

Bond Index, Heats of Formation, and Individual Bond Strengths

It may be shown that the product of the individual bond order, $P_{\mu\nu}$, and the corresponding overlap integral, $S_{\mu\nu}$, when summed over all orbitals between any pair of atoms is rotationally invariant and does not obscure the distinction between bonding and antibonding interactions, assuming the convention of choosing coordinates is consistent and understood. Further, the sums of these product-sums over all atom pairs in the individual molecules have been found to be directly proportional to the heats of formation of the molecules. That is to say for hydrocarbons,

$$\Delta H_f^A = a\beta_{\text{CH}} \sum (\text{all CH bonds})\, P_{\mu\nu} S_{\mu\nu} + b\beta_{\text{CC}} \sum (\text{all CC bonds})\, P_{\mu\nu} S_{\mu\nu} \tag{1}$$

or in abbreviated form, $\Delta H_f^A = a \sum(\text{CH}) + b \sum(\text{CC})$, where ΔH_f^A is the heat of formation of the gaseous hydrocarbon from its atoms at 0 °K, corrected for zero-point energy content, and β_{CH} and β_{CC} are the atom dependent resonance integral parameters.

The details of data compilation and of the correlations carried out may be summarized as follows. The actual interatomic distances and angles for a majority of the 18 hydrocarbons considered were obtained from the Chemical Society compilation [8]. Data for the remaining compounds: propane, isobutane, neopentane, isobutene, cyclobutane, and bicyclobutane were obtained from Refs. [9–14], respectively. Heats of formation were obtained from the A.P.I.

compilation [15], except for cyclopropane and cyclobutane which were computed from heat of combustion data at 298.16 °K from Refs. [16] and [17], respectively, and for bicyclobutane and naphthalene where the heats of formation at 298.16 °K were obtained from Refs. [18] and [19]. The corrections to 0 °K for the latter four compounds were accomplished by using the temperature corrections for propylene, isobutylene, 1,3-butadiene and benzene (with statistical correction $(3n\text{-}5)_{\text{naphthalene}}/(3n\text{-}5)_{\text{benzene}}$), respectively. The heats of formation of carbon and hydrogen atoms at 0 °K were taken as 170.39 and 51.62 kcal/mole [20].

Zero-point energies for methane, ethylene, acetylene, benzene, and allene were obtained from Ref. [7]. The propylene, methylacetylene, cyclopropane, and diacetylene ZPE values were computed from their fundamental frequencies [21] as were those for ethane, propane, isobutane, and neopentane [22], isobutene [23], cyclobutane [24], bicyclobutane [14], 1,3-butadiene [25], and naphthalene [26].

Employing the Original CNDO/2 *Parameters and the Experimentally Determined Structures*, the constant coefficients *a* and *b* of Eq. (1) were computed by least squares fitting of the data for the basic set: methane, ethane, ethylene, acetylene, 1,3-butadiene, and benzene. Hydrogen-hydrogen interactions, as expected, were found to be very small for all molecules examined and were neglected: typically $\sum(\mathrm{HH})/\sum(\mathrm{CH})$ is 3×10^{-4}. In Fig. 1, values of $\Delta H_f^A/\sum(\mathrm{CH})$ are plotted *vs.* the corresponding $\sum(\mathrm{CC})/\sum(\mathrm{CH})$ quantities. The line is the linear least squares solution for the basic set to Eq. (1). The intercept, *a*, and the slope, *b*, for Fig. 1 are respectively -10.140 and -6.230 kcal/eV. With these parameters and the summed products $\beta P_{\mu\nu} S_{\mu\nu}$, over all CH and CC bonds, the theoretical heats of formation from the constituent atoms can be computed. The standard deviation between the calculated and experimental values is 0.8% of the root-mean-square of the experimental ΔH_f^A values, or 7 kcal/mole for the basic set. Most of this deviation can be traced to acetylene whose deviation is 14 kcal/mole: the *SD* for the other compounds without refitting is 4 kcal/mole. This is not surprising since acetylene has previously been noted to be poorly represented in the CNDO method. For example, in a total energy-heat of formation correlation it could not be satisfactorily accommodated despite substantial parameter and structural freedom adjustments [7].

The agreement is somewhat poorer when the remaining compounds, not included in the basic set are examined. The *SD* is 1.5% of the *RMS* or ~18 kcal/mole. However, within this group are several compounds containing *sp*-hybrid carbons whose behavior parallels that of acetylene, and some small ring compounds for which the CNDO method appears unable to take full account of strain and for which, as well, the heat and structural data is least reliable. Diacetylene, not shown in the figure, is an interesting example of the former group. Upon what corresponds to a long extrapolation, C_4H_2 is predicted to have $\Delta H_f^A = 739$ kcal/mole. While no direct heat estimate is available, from an empirical additivity relationship based on mass spectrometric observations, a value was obtained at 298 °K [27], which yields $\Delta H_f^A = 703$ kcal/mole. The difference corresponds to somewhat more than twice the deviation noted for C_2H_2. At the same time, it is important to note that when these two recognized classes of deviates are removed, the other hydrocarbons are correlated as well

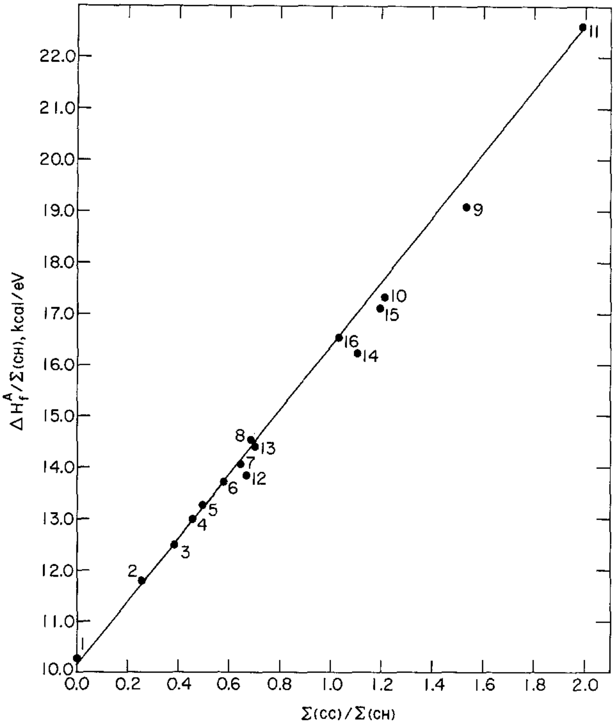

Fig. 1. $\Delta H_f^A/\sum(\mathrm{CH})$ *vs.* $\sum(\mathrm{CC})/\sum(\mathrm{CH})$. Hydrocarbon ($\Delta H_f^A$ in kcal/mole): *1* methane; *2* ethane; *3* propane; *4* isobutane; *5* neopentane; *6* ethylene; *7* propylene; *8* isobutene; *9* acetylene; *10* methylacetylene; *11* benzene; *12* cyclopropane; *13* cyclobutane; *14* bicyclobutane; *15* allene; *16* 1,3-butadiene

as those employed as standards. Even naphthalene, which requires what corresponds to a long extrapolation (it has a $\sum(\mathrm{CC})$ value almost twice that of any other compound considered), is correlated by a ΔH_f^A value only 5 kcal/mole, out of 2200, away from the experimental value.

As a further illustration of the usefulness of the presently proposed bond strength index, individual bonds of hydrocarbons can be examined. For the individual C–H bonds in methane, propane (1°–H), ethane, propane (2°–H), and isobutane (3°–H), $\sum(\mathrm{CH})$ equals -10.200, -10.090, -10.033, -9.905, and -9.635 respectively. These indices when multiplied by a should yield estimates of the energies of the particular C–H bonds. The estimates are respectively 103.4, 102.3, 101.7, 100.4, and 97.7 kcal/mole. Within this series, the order of the bond strengths is reproduced accurately, but, not surprisingly, the difference between the strongest and weakest bond (5.8 kcal/mole) is only about half that observed experimentally. Cottrell [28] reports bond dissociation energies of 101.5, 99.5, 96, 93.3, and 89.9; when these values are plotted against the corresponding $a\sum(\mathrm{CH})$-quantities, a straight line is obtained with standard deviation from the linear correlation of 0.9 kcal/mole. The fact that unit slope is not obtained is not unexpected since the bond index is for the hydrocarbon alone and neglects such effects as hyperconjugative stabilization and geometrical relaxation in the radicals which might tend to produce a wider dissociation range. Interestingly, these radical effects are predicted to parallel quite well the C–H bond strengths. In view of the successful correlation of the total of all bond energies (i.e., ΔH_f^A), it is not unreasonable to expect that adjustment based upon calculations of the bond indices in radicals whose geometry was known would yield more accurate values for the individual bonds. Whether these individual bond effects would be as relatively accurate as the ΔH_f^A values is considered in the analysis of the bond-index correlation which follows.

Analysis of the Bond Index-Molecular Energy Correlation

Recognition of the high quality of correlation between the bond index sums and heats of formation of a wide variety of hydrocarbons of apparently quite different structural, hybridization and chemical properties prompts the question, why? How does a measure which depends explicitly only upon two-atom effects correlate molecular energies which have important single-atom (one-center) contributions as well?

An informative way of resolving these questions may be had through consideration of the terms which constitute the total energy within the CNDO framework, coupled with an analysis of the successful correlation of the total energies of a more limited series of hydrocarbons previously reported [7].

The total energy of a molecule in the CNDO construction may be separated into one- and two-center interaction contributions

$$E_{\text{tot}} = \sum_{\text{A}} E_{\text{A}} + \sum_{\text{A}<\text{B}}\sum E_{\text{AB}} \tag{2}$$

where

$$E_{\text{A}} = \sum_{\mu}^{\text{A}} P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu \neq \nu}^{\text{A}} \sum^{\text{A}} \left(P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^{2} \right) \gamma_{\text{AA}} \tag{3}$$

is the energy due to atom A. The notation follows Ref. [1]: $U_{\mu\mu}$ is the atomic matrix element of the one-electron Hamiltonian including the core potential of the atom upon which the orbital ϕ_μ is centered and γ_{AA} and γ_{AB}, below, are the one- and two-center electron repulsion integrals.

The two atom energy is conveniently divided into three parts [29],

$$E_{\text{AB}} = E_{\text{AB}}^{(1)} + E_{\text{AB}}^{(2)} + E_{\text{AB}}^{(3)}, \tag{4}$$

where

$$E_{\text{AB}}^{(1)} = 2 \sum_{\mu}^{\text{A}} \sum_{\nu}^{\text{B}} P_{\mu\nu} S_{\mu\nu} \beta_{\text{AB}} \tag{5}$$

is proportional to the bond index terms for the CH and CC atom pairs proposed empirically above. (An incompletely analogous but usefully recognized precursor to the bond index form and hence to Eq. (5) is to be found in the definition of the total binding energy in overlap included-π-electron theory for hydrocarbons from Mulliken overlap population analysis, i.e., $2\Gamma \sum P_{\mu\nu}$, where

$\Gamma = \beta - \alpha S$ and the sum is over all bonds [30].)

$$E_{AB}^{(2)} = -\frac{1}{2}\sum_{\mu}^{A}\sum_{\nu}^{B} P_{\mu\nu}^{2}\gamma_{AB} \qquad (6)$$

which represents the stabilization due to exchange interactions is, interestingly, of the same form as the Wiberg bond index [5] and would be identical, except for the factor $-\frac{1}{2}$, were all two-electron integrals for the molecule, γ_{AB}, the same. The third term which contains the electron-electron, nucleus-nucleus and cross-charge species electrostatic interactions is,

$$E_{AB}^{(3)} = P_{AA}P_{BB}\gamma_{AB} + Z_A Z_B/R_{AB} - (P_{AA}Z_B + P_{BB}Z_A)\,\gamma_{AB}\,. \qquad (7)$$

From computed CNDO molecular energies of atomization of the same size, yet less constitutionally varied hydrocarbon set: methane, ethane, propane, butane, ethylene, and benzene, Wiberg [7] could demonstrate an excellent correlation with heats of formation.

$$\Delta E(\text{atom}) = n_C E(\text{C}) + n_H E(\text{H}) - E_{\text{tot}} \qquad (8)$$

where E(C) and E(H) are the free atom energies and

$$\Delta H_f^A = 218.01\,\Delta E(\text{atom}) + 35.28\,. \qquad (9)$$

The statistics of fitting are here $SD/RMS = 0.2\%$. The least square correlation which yields the coefficients of Eq. (9), it should be pointed out, is based upon calculations using $\frac{1}{2}(I+A)$, the diagonal matrix parameters, and β parameters for carbon and hydrogen optimized for reproduction of energies and geometries for methane, ethane, and ethylene, and employs the calculated equilibrium geometries for all the basic set. These measures are, however, as was mentioned previously, incapable of making the fit for acetylene comparable acceptable.

In order to examine the differences caused by abandonment of the original CNDO/2 parameters and observed molecular geometries, and to facilitate the comparisons to be drawn, the bond-index correlation previously described was redrawn employing the Wiberg parameters. For $\frac{1}{2}(I+A)_{2sC}$, $\frac{1}{2}(I+A)_{2pC}$, β_C, and β_H of 10.3, 6.3, -17.5, and -10.0 eV rather than 14.051, 5.572, -21, and -9 eV, a and b for Eq. (1) are -11.510 and -7.261 kcal/eV, respectively and the $SD/RMS = 0.9\%$ for the original bond-index set, including acetylene. The molecular geometries were maintained as the experimentally determined ones with the expectation that changes here, except perhaps for acetylene, would be minor and dispersive. It is apparent that the goodness of fitting as regards the bond-index correlation is not improved by variation of parameters to those which improve the total energy correlation. The increased values of the coefficients reflects the general decrease in $E_{AB}^{(1)}$ (in fact, in E_{AB} itself) upon the prescribed parameter changes.

We may now transform Eqs. (1) and (9) into comparable units and forms.

$$\Delta H_f^A = (-11.510)\sum(\text{CH})_{\text{eV}} + (-7.261)\sum(\text{CC})_{\text{eV}} \qquad (10a)$$

$$= -313.18\sum(\text{CH})_{\text{a.u.}} - 197.57\sum(\text{CC})_{\text{a.u.}} \qquad (10b)$$

and, dropping the subscripts and summation indices on the partitioned two-center energy terms,

$$\begin{aligned} \Delta H_f^A &= 218.01\,\Delta E(\text{atom})_{\text{a.u.}} + 35.28 \\ &= -218.01\{\textstyle\sum^{\text{C}} E_{\text{C}} + \sum^{\text{H}} E_{\text{H}} + 2\sum(\text{CH}) + 2\sum(\text{CC}) \\ &\quad + \textstyle\sum E^{(2)} + \sum E^{(3)} - n_{\text{C}}E(\text{C}) - n_{\text{H}}E(\text{H})\}_{\text{a.u.}} + 35.28\,. \end{aligned} \tag{11}$$

Tables 1 and 2 contain digests of the various separated quantities and pertinent derivative quantities of Eqs. (10) and (11). Several important observations may be quickly made.

The one-center contributions of the carbon and hydrogen atoms are remarkably constant *per atom* over the wide variety of hydrocarbons considered. The average values of E_{C} vary at most by a few tenths-of-a percent in contrast to electron distribution differences which are much larger: e.g., $2s$ orbital densities vary by 10% or more. The average value of E_{C} per carbon atom over the set employed to obtain the bond indices is 141.56 ± 0.17 eV (5.2025 ± 0.0062 a.u.) and the average value of E_{H} per H atom is 12.22 ± 0.06 (0.4491 ± 0.0022 a.u.) over the same set, employing the Wiberg parameters. With the Wiberg set, the deviations are, of course, smaller, again because acetylene is ignored. Employing the original CNDO/2 parameters, the deviations are slightly larger (~ 2 times as large); the E_{C} and E_{H} values are respectively 2.19 eV more negative and 0.06 eV more positive.

In general, the one-center, the two-center energy contributions, and the total energy, and, as well, the bond index values are smaller employing the modified CNDO parameters. This might have been expected noting the change in coefficients from Eq. (1) to Eq. (10a).

The remarkable fact emerges from examination of Table 2 that twice the value of the bond index reproduces, to within at most a few percent, the sum of the total two-center energies, both for the C–C and C–H interactions. In general, the bond index overestimates in magnitude $\sum E_{\text{CC}}$; and, the greater the unsaturation of the molecule, the greater the overestimation. On the other hand, the bond index as often underestimates as overestimates $\sum E_{\text{CH}}$, and is more precise in general in its estimation. It is clear at this point that the bond index proposed here is much more appropriate a measure of the two-center or formal bonding properties of a molecule than is any prescription based upon $P_{\mu\nu}^2$-values, which constitute as the explicit SCF variables the quantity $\sum E^{(2)}$(see Eq. (6)), or for that matter, atom charge combinations such as are found in $\sum E^{(3)}$, since the latter terms, as the mathematics above reveals, at best, always cancel, or at worst are both insignificantly small. In physical fact, it is always a matter of cancellation between $\sum E^{(2)}$ and $\sum E^{(3)}$, each being a not insignificant fraction the size of $\sum E^{(1)}$. At any rate, neither the electrostatic interactions of $\sum E^{(3)}$, the exchange terms of $\sum E^{(2)}$, nor certainly their sum can reasonably be taken as representative of the primary bonding effects in normal covalent molecules.

Although not explicitly shown in Table 2, it may easily be verified that the value of $\sum(\text{CH})$ divided by the number of classical CH bonds is essentially invariant over all the hydrocarbons considered. The quality of invariance is not quite that of the one-center energies previously examined; for the basic set

Table 1. *One-center contributions to the total energies, total energies and heats of formation*[a]

Molecule	$-\sum E_C$	$-Av$	$-\sum E_H$	$-Av$	$-E_{tot}$	ΔH_f^A
CH_4	143.98	143.98	48.75	12.19	275.19	419.97
	141.75	141.75	48.67	12.17	264.16	
C_2H_6[b]	286.84	143.42	73.58	12.26	511.76	712.18
	282.82	141.41	73.44	12.24	489.89	
C_2H_4	287.67	143.83	48.71	12.18	464.36	563.44
	283.09	141.54	48.92	12.23	443.70	
C_2H_2	288.84	144.42	23.61	11.80	417.44	405.87
	283.76	141.88	24.12	12.06	397.89	
1,3-C_4H_6	574.30	143.58	73.27	12.21	890.57	1014.17
	565.75	141.44	73.53	12.26	849.04	
C_6H_6	859.61	143.27	73.92	12.32	1281.60	1370.90
	847.89	141.32	73.96	12.33	1218.66	
n-C_3H_8	429.61	143.20	98.36	12.30	748.43	1006.04
	423.94	141.31	98.07	12.26	715.33	
i-C_4H_{10}	572.73	143.18	123.04	12.30	984.94	1301.96
	—	—	—	—	—	
isobutene	573.61	143.44	97.98	12.25	938.08	1158.91
	565.75	141.44	97.72	12.22	895.38	
neo-C_5H_{12}	716.15	143.23	147.61	12.30	1221.01	1597.98
	—	—	—	—	—	
propylene	430.50	143.50	73.35	12.22	701.13	861.01
	424.37	141.46	73.33	12.22	669.32	
methylacetylene	431.54	143.85	48.29	12.07	655.08	705.44
	425.08	141.69	48.43	12.11	624.35	
allene	431.61	143.87	48.09	12.02	654.22	703.18
	425.09	141.70	48.30	12.08	623.58	
diacetylene	575.77	143.94	23.54	11.77	797.78	739
	566.82	141.71	24.08	12.04	758.07	
cyclopropane	430.35	143.45	73.30	12.22	705.33	856.68
	424.65	141.55	73.52	12.25	673.43	
cyclobutane	572.93	143.23	98.37	12.30	943.17	1160.50
	565.42	141.32	98.28	12.28	900.27	
bicyclobutane	573.41	143.35	73.62	12.27	896.80	988.74
	566.12	141.53	73.84	12.31	855.34	

[a] All E-quantities in eV, ΔH_f^A in kcal/mole. The first row for each molecule is obtained with the original CNDO/2 parameters, the second with the Wiberg parameters. Averages are per C or per H, as the case may be.

[b] The staggered configuration.

including acetylene, $2\sum(\mathrm{CH})/n_{\mathrm{CH}} = -18.40 \pm 0.30$ eV (0.6762 ± 0.0110 q. u.), employing the results from the parametrically modified calculation. The calculation with the original parameters yields a higher average with a similar deviation (-20.52 ± 0.28 eV): the Wiberg basic set with modified parameters would yield a slightly smaller average and a better average deviation, reflecting the absence of acetylene.

For all the compounds considered, in fact for all compounds of classical nature (i.e., not having hydrogen bridges), the number of classical CH bonds is equal to the number of hydrogens. Because of multiple bonding, however, the same equality is not found for the number of carbons and CC bonds. Never-

Table 2. *Two-center contributions to the total energies and bond index values*[a]

Molecule	$-\sum E_{\mathrm{CC}}$	$-2\sum(\mathrm{CC})$	R	$-\sum E_{\mathrm{CH}}$	$-2\sum(\mathrm{CH})$	R
CH_4	0	0	—	83.21	81.60	0.981
	0	0	—	73.59	72.02	0.979
C_2H_6[b]	29.77	30.17	1.013	122.64	120.87	0.986
	24.09	24.83	1.031	109.67	107.73	0.982
C_2H_4	46.46	47.50	1.022	81.95	82.09	1.002
	38.08	39.22	1.030	73.76	73.69	0.999
C_2H_2	62.84	65.52	1.043	42.13	42.70	1.014
	52.11	54.72	1.050	37.88	38.46	1.015
1,3-C_4H_6	121.72	126.75	1.041	121.66	122.74	1.009
	100.06	105.26	1.052	109.87	110.71	1.008
C_6H_6	228.02	240.43	1.054	120.52	121.35	1.007
	187.70	200.34	1.067	109.65	110.13	1.004
n-C_3H_8	59.54	61.52	1.033	162.07	161.10	0.994
	48.35	50.52	1.045	145.11	143.92	0.992
i-C_4H_{10}	88.05	91.50	1.039	202.60	200.52	0.990
	—	—	—	—	—	—
isobutene	104.85	109.90	1.048	162.59	159.11	0.979
	86.11	91.29	1.060	145.42	142.55	0.980
neo-C_5H_{12}	115.11	119.17	1.035	244.05	241.03	0.988
	—	—	—	—	—	—
propylene	76.14	78.79	1.035	121.79	122.54	1.006
	62.42	65.18	1.044	109.05	109.84	1.007
methylacetylene	93.52	98.55	1.054	82.14	81.38	0.991
	77.25	82.26	1.065	73.33	72.77	0.992
allene	93.06	97.97	1.053	81.83	82.20	1.004
	76.78	81.67	1.064	73.31	73.74	1.006
diacetylene	156.34	166.86	1.067	42.15	43.25	1.026
	129.37	139.78	1.080	37.80	38.94	1.030
cyclopropane	79.55	82.41	1.036	122.94	123.68	1.006
	65.13	68.18	1.047	110.42	110.93	1.005
cyclobutane	110.78	112.97	1.020	162.18	161.04	0.993
	90.78	93.35	1.028	146.24	144.94	0.991
bicyclobutane	129.03	134.41	1.042	121.34	121.90	1.005
	105.80	111.43	1.053	109.76	110.06	1.003

[a] Energy and bond index values in eV, ratios (R-values, bond index/energy) are unitless. The first row for each molecule is obtained with the original CNDO/2 parameters, the second with the Wiberg parameters.

[b] The staggered configuration.

theless, there is a simple relation for the number of CC bonds, not distinguishing between types, which is linearly dependent upon the number of hydrogens and carbons in the molecule, i.e., $n_{\mathrm{CC}} = (4n_{\mathrm{C}} - n_{\mathrm{H}})/2$, and which yields a remarkably constant ratio, $2\sum(\mathrm{CC})/n_{\mathrm{CC}}$, considering the aforementioned lack of distinction. For the bond-index basic set, the ratio average is -21.20 ± 1.90 eV (-0.7791 ± 0.0698 a.u.); for the Wiberg set the corresponding values are ~ -2.5 eV greater for the average and just about the same for the average deviation, all results from the parametrically modified calculations.

We are now in a position to continue the transformation of Eq. (11). Adopting, consistently, the free atom energies for carbon and hydrogen respectively as -5.9428 and -0.5275 a.u. [7] and reporting standard rather than average deviations for the purpose of making a propogation of error analysis

$$\begin{aligned}\Delta H_f^A = &-218.01\{n_{\mathrm{C}}(0.7403 \pm 0.0079) + n_{\mathrm{H}}(0.0784 \pm 0.0034)\\ &+2\sum(\mathrm{CH}) + 2\sum(\mathrm{CC}) + \sum E^{(2)} + \sum E^{(3)}\} + 35.28\,.\end{aligned} \tag{12}$$

Expressions for n_{C} and n_{H} are obtained from the number-of-bonds relationships just discussed

$$\begin{aligned}n_{\mathrm{H}} &= (-1.4788 \pm 0.0369) \cdot 2\sum(\mathrm{CH})\,,\\ n_{\mathrm{C}} &= (-0.6418 \pm 0.0685) \cdot 2\sum(\mathrm{CC}) + (-0.3697 \pm 0.0092) \cdot 2\sum(\mathrm{CH})\,.\end{aligned} \tag{13}$$

Making the reasonable assumption that the deviations of the one-center and two-center terms are at least to the first order independent, but that the deviations between the n_{C} and n_{H} bond index terms are not, and, in addition, that an uncertainty exists in the $\Delta H_f^A - \Delta E$ relationship at least as large as that obtained upon refitting to the bond index basic set,

$$\begin{aligned}\Delta H_f^A &= (-218.0 \pm 6.1)\{(0.6104 \pm 0.0300) \cdot 2\sum(\mathrm{CH})\\ &\quad + (0.5249 \pm 0.0510) \cdot 2\sum(\mathrm{CC}) + E^{(2)} + E^{(3)}\} + 35.3 \pm 9.1\\ &= (-266.1 \pm 20.5)\sum(\mathrm{CH}) + (-228.9 \pm 28.7)\sum(\mathrm{CC})\\ &\quad + (-218.0 \pm 6.1)\left(\sum E^{(2)} + \sum E^{(3)} - (0.16 \pm 0.05)\right).\end{aligned} \tag{14}$$

It is clear that Eq. (14) very strongly resembles Eq. (11) especially when the non-identity of basic sets used and the very rough estimation of uncertainty in the $\Delta H_f^A - \Delta E$ relationship are recognized. Properly, the deviations within the sets used to determine the slope and intercept should have been considered. As well, the coefficients of Eq. (11) are presented without error estimates. With regard to the intercept in Eq. (14), it is of interest to note that $E^{(2)} + E^{(3)}$ is generally but not always positive for the hydrocarbons, the result of larger positive C–C contributions than negative or small positive C–H contributions. In fact, the average value of these residual two-center terms over the original bond index basic set is ~ 3.5 eV or 0.13 a.u., which nicely cancels the original intercept value. Caution is advised, however, in placing physical interpretation upon this cancellation because, although the $E^{(2)} + E^{(3)}$ sums over the molecule are generally small, the values do fluctuate. The largest values encountered are for ring compounds, e.g., in benzene the value is > 3 times that of the average of the other basic set molecules, a fact which will be examined below.

On obvious refinement of the additivity of effects analysis just detailed is in order. The number of CC bonds in a molecule, independent of type, was employed to determine the average contribution to $\sum(\mathrm{CC})$, despite easy recognition from Table 2 that σ- and π-bonds do indeed differ. The statistics, based on a simplistic, non-physical assumption of randomness of deviation are capable of partially obscuring the difference. The effect of this difference on the transformation of Eq. (11) may be fairly easily discerned as follows. The number of CC σ-bonds, π-bonds, counted as localized even where conjugation is possible, and CH bonds (all σ-bonds for the molecules under discussion) are related by

$$\begin{aligned} n^{\sigma}_{\mathrm{CC}} &= n_{\mathrm{C}} - (1-r)\,, \\ n^{\pi}_{\mathrm{CC}} &= n_{\mathrm{C}} + (1-r) - \tfrac{1}{2} n_{\mathrm{CH}}\,, \end{aligned} \tag{15}$$

where r is the number of rings formed by the σ-bond framework. The relation for the total number of CC bonds previously derived is satified, and, as well, the fact that $n_{\mathrm{CH}} = n_{\mathrm{H}}$ is usefully recalled. We adopt the form

$$2 \sum (\mathrm{CC}) / (n^{\sigma}_{\mathrm{CC}} + f\, n^{\pi}_{\mathrm{CC}}) = k \tag{16}$$

where k and fk are the average bond index contributions per σ- and π-bond, respectively. Least squares fitting to Eq. (16) of the bond index basic set, which contains of the five molecules contributing to the statistics (methane has no CC bond, of course), four of widely variable π bonding characteristics, yields the following results. The coefficients k and f are respectively -26.17 eV and 0.538 and the mean and standard deviations are, respectively, 1.05 and 1.24 eV (contrast to -21.20 eV for the previous average bond index contribution and 1.90 and 2.26 eV for the respective deviation measures). That the deviations decrease substantially (*SD* by much more than the factor to be expected from inclusion of the extra parameter, f) indicates the important difference which exists between the σ- and π-bonds; that the deviations are still as large as they are may be taken to indicate that differences in the bonds, both σ and π, are larger than the differences which exist among the CH bonds over the same molecules.

Proceeding as above with substitution of the improved n_{C}-relationship from Eqs. (15) and (16)

$$\begin{aligned} \Delta H_f^A = {} & (-218.0 \pm 6.1) \Big\{ (0.6927 \pm 0.0237) \cdot 2 \sum (\mathrm{CH}) \\ & + (0.4996 \pm 0.0243) \cdot 2 \sum (\mathrm{CC}) + (0.7403 \pm 0.0079) \left(\frac{1-f}{1+f} \right) (1-r) \\ & + \sum E^{(2)} + \sum E^{(3)} \Big\} + 35.28 \end{aligned} \tag{17}$$

$$\begin{aligned} = {} & (-302.0 \pm 18.8) \sum (\mathrm{CH}) + (-217.8 \pm 16.7) \sum (\mathrm{CC}) \\ & + (-218.0 \pm 6.1) \, \{ (0.22 \pm 0.01)(1-r) \\ & + \sum E^{(2)} + \sum E^{(3)} - (0.16 \pm 0.05) \}\,. \end{aligned} \tag{18}$$

The correspondence between the bond index and total energy dependences of ΔH_f^A is now abundantly clear, down to the fine detail of cancellations in the intercept term of the latter relationship. For the chain compounds, where r is zero and the first and last term of the intercept cancel, only small $\sum E^{(2)} + \sum E^{(3)}$ are generally encountered. For the unstrained rings, the latter terms are relatively larger but are cancelled by the combination of the first and last intercept terms. Interestingly, for naphthalene, not shown in the Tables, $\sum E^{(2)} + \sum E^{(3)}$ is essentially twice that for benzene (26.6 eV, employing the original parameters *vs.* 12.4 eV), an increase which is properly compensated for by the increase of r

from one to two. In the cases of strained rings, the bond index somewhat more closely approximates the two-center energy sum. Therefore, were the last terms of Eq. (18) (in curly brackets) included in the bond index correlation for these compounds, where ΔH_f^A is already overestimated, the apparent deviations would increase.

On the other hand, the compounds with *sp*-hybrid carbons all show fairly substantial positive $\sum E^{(2)} + \sum E^{(3)}$ values, and since there are no rings involved, inclusion of the last term of Eq. (18) would tend to make the correlation appear better. These arguments should of course not be carried too far; the coefficients of Eq. (18) are not identically those of Eq. (11), nor are either free of uncertainty, nor for that matter, are the $\sum E^{(2)} + \sum E^{(3)}$ values for the "normal" hydrocarbons vanishingly small.

Finally, the reverse transformation, of Eq. (10b) with the model relationships Eqs. (13), (15), and (16), to generate a bond additivity relationship for the heats of the form, $\Delta H_f^A = A n_{\mathrm{CH}} + \sum_{\text{bond type}} B_i n_{\mathrm{CC}}^i$, provides another perspective on the individual differences which must exist among the various hydrocarbon bonds. With Eq. (13), A and B are respectively 104.4 ± 2.6 and 77.0 ± 8.2 kcal/mole. Not unexpectedly, the heats of the saturated hydrocarbons are uniformly underestimated when this relationship is used, while the heats of the highly unsaturated molecules having only weak or non-existent conjugation properties are overestimated. With Eq. (16), A is unchanged and B_σ and B_π are respectively 95.0 ± 6.9 and 51.1 ± 3.7 kcal/mole. Application of this relationship improves the overall fitting, mainly through improvements for the unsaturated and conjugation-stabilized hydrocarbons. In comparison with similar relationships developed entirely on an empirical basis [31], it is apparent that the CH bonds are satisfactorily represented but that once distinction is made between σ- and π-CC-bonds, B_σ will be too large for the longer, weaker alkane bonds and B_π will be too small for systems where strong conjugation among π-bonds, assumed localized for counting, is possible. It should of course be stressed that these recognizable inconsistencies only arise when the very approximate counting relationships, Eqs. (13), (15), and (16), are introduced. The bond orders of Eqs. (1) and (10b) obviously recognize these and the even finer differences which exist among the hydrocarbon bonds.

The question of whether individual bond effects will be well correlated by the bond index treatment, assuming relaxation upon breaking of the bond in question is properly considered, would appear to deserve an affirmative answer, with one qualification. This qualification may be expressed in terms of the changes in slope and intercept noted in the $\Delta H_f^A - \Delta E$ correlation for various radicals and ions [7], compared to the results for the hydrocarbons from which these species may be considered to arise by scission. If these differences are functions solely of different mean one- and two-center interactions which are as well characterized with respect to deviations, then, at worst, different coefficients in the bond index correlation might be required. If, however, the same or similar patterns of regularity do not exist as in the parent hydrocarbons, a modified form of the bond index equation might be required. The alkane bond-strength correlation described above seems cause for optimism in this regard.

The successes of the bond index correlation of heats of formation and cross correlation of CNDO/2 binding energies suggests for future work a means to improve the most arbitrary and thereby most objectionable feature of CNDO/2 parametrization, i.e., the β-values. In contrast to the diagonal matrix elements which have physical meaning as ionization and electron attachment energies, and the S- and γ-quantities which are computed properly as integrals, albeit over limited basis sets, the β-values were chosen to reproduce electronic energy spacings for the highest filled to unfilled (virtual) MO's from rather poor SCF functions for various diatomics. What is now possible, in light of the good correlation of heats of formation, is to extract the new β's ($a\beta_{\mathrm{CH}}$ and $b\beta_{\mathrm{CC}}$) and through a self-consistency procedure produce values which have physical reality in the sense of relating to a fundamental molecular property. Justification of the procedure is readily available in that the analysis already carried out indicates essential freedom of the heats of all one-center and other two-center interaction contributions beyond those involving β's as parameters. That the relationship is linear in β's suggests, further, that analysis of the self-consistency procedure for their computation may yield other important information on hydrocarbon bonding.

Extension of these investigations to molecules containing other than carbon and hydrogen is also in progress; the results of some of this work in oxygen-containing molecules where hydrogen bonding provides several additional features of covalent and ionic interactions not present in the hydrocarbons has been detailed [32]. Extraction of heteroatom β's, in the same manner as just described for the hydrocarbons, is under consideration.

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