Charge Distributions and Chemical Effects. 14.[1] On Molecular Energies Derived from Additivity Schemes Involving the Charges of the Bond-Forming Atoms

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Abstract: A simple equation has been developed for predicting binding energies of saturated hydrocarbons from the knowledge of their ^{13}C NMR spectra only. The study of the energy of atomization at the hypothetical vibrationless state, ΔE_a^*, in terms of bond contributions (ϵ_{ij}) indicates that the latter can be conveniently approximated by a Taylor expansion of some function, $\epsilon_{ij} = \epsilon_{ij}(Q_i,Q_j)$, of the electron populations Q_i, Q_j of the bond-forming atoms i and j. For saturated hydrocarbons $C_nH_{2n+2-2m}$ containing m six-membered rings ($m = 0$–5) it follows then from the equation $\Delta E_a^* = \Sigma\epsilon_{ij}$ and from the relationship between ^{13}C NMR shifts and carbon net charges that $\Delta E_a^* = (1 - m)\Delta E_a^*(C_2H_6) + (n - 2 + 2m)\,[\Delta E_a^*(C_2H_6) - \Delta E_a^*(CH_4)] + \lambda_1\Sigma N_{CC}\delta + \lambda_2[(n - 2 + 2m)\delta(CH_4) + \Sigma\delta]$, where δ = shift relative to ethane, N_{CC} = number of CC bonds formed by the C atom whose shift is δ, and λ_1 and λ_2 are adjusted parameters. This two-parameter bond-energy scheme is equally applicable to acyclic hydrocarbons ($m = 0$) as to polycyclic compounds, such as bicyclo[2.2.2]octane, adamantane and diadamantane, without requiring any "ring-strain" correction, thus differentiating this approach from others which fail whenever used for cyclic structures if they do not include strain-energy terms. The latter point is briefly examined in terms of zero-point and thermal energy contributions.

Any attempt like the present one directed toward the description of molecular properties (enthalpies of formation, binding energies, etc.) in terms of bond contributions rests basically upon the concept of molecules viewed as assemblies of "chemical bonds". In this perspective, the "molecular energy" (which remains to be defined more precisely) of saturated hydrocarbons can, in principle, be estimated from additivity rules.

In practice, however, simple additivity schemes assuming that the contribution of each CC and CH bond is the same in any molecule containing these bonds fail to give satisfactory results, thus creating the need for corrections. In the bond energy scheme studied by Laidler,[2] for example, the energy terms of primary, secondary, and tertiary CH bonds are not identical, whereas the CC terms are presumed constant. Tatevskii's modification[3] is based on the assumption that not only should the CH bonds in paraffins be classified according to their immediate environment but that the CC bonds should be similarly classified. Here, of course, increasing sophistication and the accompanying proliferation of parameters improve the results but add little to the understanding of the intimate reasons which differentiate the various CC and CH bonds according to their molecular environment. The situation is somewhat different with theories involving steric effects[4] because of the physical models underlying them. It remains that once the principle of describing a particular topological situation by a parameter is accepted, the success of this type of approach for evaluating departures from simple additivity depends on the number of different structural features which are considered and parameterized in order to cover an adequate body of compounds.

The present additivity scheme is different, in that changes in bond properties are studied in terms of inductive effects. While each bond is still regarded as a separate unit, the present treatment recognizes that, because of some charge transfer from neighboring bonds, a given bond is not exactly the same in the various environments. Ultimately, the changes in bond properties are evaluated in terms of charges allocated to the bond-forming atoms.

Bond energy schemes involving explicitly a charge dependence for studying enthalpies of formation at 25 °C were presented recently,[5,6] but these studies differ considerably one from another in the fine tuning of the bond contributions in terms of charges. The present study is still different in that it avoids unnecessary difficulties, such as those arising from internal rotations which are more or less free in some cases and hindered in others. This is simply done by studying the molecules at 0 K. Moreover, zero-point energies are explicitly taken into account, as these energies, like the thermal ones, cannot fairly be apportioned among the bonds since they are not truly additive properties nor can they be regarded as resulting from chemical binding.

Working Formulas and Hypotheses

Bond-energy schemes are commonly expressed in terms of enthalpy H. The disadvantage of such a practice is that it leads to systematic errors, e.g., in the evaluation of ring strain.[7] In the study of a property of the isolated molecule, energies must be defined in terms of energy, E, and not of enthalpy.

For saturated hydrocarbons containing m rings

$$C_nH_{2n+2-2m} \rightarrow nC(g) + (2n + 2 - 2m)H(g)$$

the relation between atomization enthalpies, ΔH_a, and energies, ΔE_a, is

$$\Delta H_a = \Delta E_a + (3n + 1 - 2m)RT \qquad (1)$$

with

$$\Delta H_a = n\Delta H_f^\circ(C) + (2n + 2 - 2m)\Delta H_f^\circ(H) - \Delta H_f^\circ \qquad (2)$$

where ΔH_f° = enthalpy of formation of the hydrocarbon under consideration, at some temperature T (usually 25 °C, gas), and $\Delta H_f^\circ(C)$ and $\Delta H_f^\circ(H)$ are the enthalpies of formation of gaseous carbon and hydrogen, respectively, at the same temperature. Finally, the energy of atomization at the hypothetical vibrationless state, ΔE_a^*, is given by[7]

$$\Delta E_a = \Delta E_a^* - \sum^{9n-6m} F(\nu_i,T) + (9n - 6m)RT/2 \qquad (3)$$

where $\Sigma F(\nu_i,T)$ is the vibrational energy corresponding to the fundamental frequencies ν_i.

It follows from eq 1–3 that

$$\begin{aligned}\Delta E_a^* = n[\Delta H_f^\circ(C) - 5RT/2] \\ + (2n + 2 - 2m)[\Delta H_f^\circ(H) - 5RT/2] \\ + \sum^{9n-6m} F(\nu_i,T) + 4RT - \Delta H_f^\circ \qquad (4)\end{aligned}$$

The vibrational energy may be separated into a zero-point energy term and a thermal-energy term. In the harmonic oscillator approximation, the zero-point energy is equal to

$$\mathrm{ZPE} = N_{\mathrm{Av}} \sum_i h\nu_i/2 \tag{5}$$

The thermal-energy term is the energy of 1 mol of gas in excess of that which it would have if all molecules were in the lowest energy level, i.e., with E = total energy of the system at some temperature T and E_0 = energy with all molecules in their lowest energy level,

$$E_{\mathrm{thermal}} = E - E_0 = 3RT + E_{\mathrm{vib}}$$

for nonlinear molecules. Consequently, in terms of enthalpy, the thermal contribution is given by

$$H_{\mathrm{T}} - H_0 = 4RT + E_{\mathrm{vib}} \tag{6}$$

It follows from eq 6 that $\Sigma F(\nu_i,T) + 4RT = \mathrm{ZPE} + H_{\mathrm{T}} - H_0$. Equation 4 can now be written

$$\begin{aligned}\Delta E_{\mathrm{a}}^* = n[\Delta H_{\mathrm{f}}^\circ(\mathrm{C}) - 5RT/2] \\ + (2n + 2 - 2m)[\Delta H_{\mathrm{f}}^\circ(\mathrm{H}) - 5RT/2] \\ + \mathrm{ZPE} + (H_{\mathrm{T}} - H_0) - \Delta H_{\mathrm{f}}^\circ\end{aligned} \tag{7}$$

The experimental ΔE_{a}^* discussed in the next section were derived from eq 7, using enthalpy values[8] at T = 298.16 K, i.e., $\Delta H_{\mathrm{f}}^\circ(\mathrm{C})$ = 170.89 and $\Delta H_{\mathrm{f}}^\circ(\mathrm{H})$ = 52.09 kcal/mol. Zero-point energies were obtained from vibrational spectra (eq 5) using experimental frequencies whenever available, while the nonobserved frequencies were extracted from data calculated by means of an appropriate model. The experimental $H_{\mathrm{T}} - H_0$ values were taken from literature. They include, of course, all effects which may arise from more or less hindered internal rotations. For rigid molecules, such as adamantane, the thermal contributions were calculated using eq 6, whereby the vibrational thermal terms were obtained from Einstein's equation

$$E_{\mathrm{vib}} = N_{\mathrm{Av}} \sum_i h\nu_i \exp(-h\nu_i/kT)/[1 - \exp(-h\nu_i/kT)] \tag{8}$$

We can now focus attention on the hypotheses involved in the present work. To begin with, it is postulated that the energy of atomization at the hypothetical vibrationless state can be apportioned into energy terms, ϵ_{ij}, referring to the individual bonds ij, i.e.,

$$\Delta E_{\mathrm{a}}^* = \sum \epsilon_{ij} \tag{9}$$

Next, it is postulated that the individual bond-energy terms are some function

$$\epsilon_{ij} = \epsilon_{ij}(Q_i,Q_j) \tag{10}$$

of the total electron populations Q_i and Q_j of the bond-forming atoms i and j.

Equations 9 and 10 really close the description of the working hypotheses, as no other effects, such as stabilization energies, destabilization energies, steric effects, or ring-strain (for six-membered rings), need be invoked in the forthcoming treatment.

Charge Dependence of ΔE_{a}^*

Provided that for a given bond ij the variations in Q_i and Q_j due to changes in molecular environment are small, the expansion of ϵ_{ij} (eq 10) in a Taylor series limited to the first order yields

$$\epsilon_{ij} = \epsilon_{ij}{}^0 + \Delta Q_i \left(\frac{\partial \epsilon_{ij}}{\partial Q_i}\right)_{Q_i{}^0,Q_j{}^0} + \Delta Q_j \left(\frac{\partial \epsilon_{ij}}{\partial Q_j}\right)_{Q_i{}^0,Q_j{}^0} \tag{11}$$

In terms of net (i.e., $Z - Q$) atomic charges q_i and q_j, whereby $\Delta q = -\Delta Q$, eq 11 takes the form

$$\epsilon_{ij} = \epsilon_{ij}{}^0 - \Delta q_i \left(\frac{\partial \epsilon_{ij}}{\partial Q_i}\right)_0 - \Delta q_j \left(\frac{\partial \epsilon_{ij}}{\partial Q_j}\right)_0 \tag{12}$$

Following this argument, we write for the CC bonds

$$\epsilon_{\mathrm{CC}} = \epsilon_{\mathrm{CC}}{}^0 + a(\Delta q_{\mathrm{C}i} + \Delta q_{\mathrm{C}j}) \tag{13}$$

and, for the CH bonds,

$$\epsilon_{\mathrm{CH}} = \epsilon_{\mathrm{CH}}{}^0 + b\Delta q_{\mathrm{C}} + c\Delta q_{\mathrm{H}} \tag{14}$$

where a, b, and c represent the appropriate $-(\partial\epsilon_{ij}/\partial Q_i)_0$ values of eq 12 and are treated here in empirical manner. It now becomes necessary to select a substance of reference for defining both the ϵ^0's and the Δq's. Here, $\epsilon_{\mathrm{CC}}{}^0$ and $\epsilon_{\mathrm{CH}}{}^0$ are defined with respect to the ethane CC and CH bonds and, consequently, Δq_{C} and Δq_{H} are expressed relative to the C, viz., H, net atomic charges of ethane. Now, of course, the absolute values of net atomic charges, including those of ethane, are not known,[9] nor are they required in this study. Indeed, only their ordering in a relative scale is of immediate concern. A practical scale[9] is defined by letting the ethane C net charge = 1 arbitrary unit and, hence, the ethane H net charge = $-\frac{1}{3}$ arbitrary unit. It is then $\Delta q_{\mathrm{C}} = q_{\mathrm{C}} - 1$ and $\Delta q_{\mathrm{H}} = q_{\mathrm{H}} + \frac{1}{3}$.

It is now easy to calculate ΔE_{a}^* from eq 9, 13, and 14. For hydrocarbons $\mathrm{C}_n\mathrm{H}_{2n+2-2m}$, in which the number of CC bonds is $n - 1 + m$, their contribution is $\Sigma\epsilon_{\mathrm{CC}} = (n - 1 + m)\epsilon_{\mathrm{CC}}{}^0 + a\Sigma N_{\mathrm{CC}}\Delta q_{\mathrm{C}}$, where N_{CC} = the number of CC bonds formed by the C atom to which Δq_{C} refers. Similarly, remembering that the number of CH bonds is $2n + 2 - 2m$, their contribution is $\Sigma\epsilon_{\mathrm{CH}} = (2n + 2 - 2m)\epsilon_{\mathrm{CH}}{}^0 + b\Sigma N_{\mathrm{H}}\Delta q_{\mathrm{C}} + c\Sigma\Delta q_{\mathrm{H}}$, where N_{H} = the number of H atoms bonded to the C atom of which Δq_{C} is computed, i.e., $N_{\mathrm{H}} = 4 - N_{\mathrm{CC}}$. Finally, observing that $\Sigma\Delta q_{\mathrm{H}} = \Sigma q_{\mathrm{H}} - (2n + 2 - 2m)q_{\mathrm{H}}{}^{\mathrm{ref}} = -\Sigma q_{\mathrm{C}} + (2n + 2 - 2m)/3 = -\Sigma\Delta q_{\mathrm{C}} - n + (2n + 2 - 2m)/3$, the summation over all the ϵ_{ij} terms yields eq 15, where $\epsilon_{\mathrm{CC}}{}^0 + 6\epsilon_{\mathrm{CH}}{}^0 = \Delta E_{\mathrm{a}}^*(\text{ethane})$.

$$\begin{aligned}\Delta E_{\mathrm{a}}^* = (1 - m)\Delta E_{\mathrm{a}}^*(\text{ethane}) \\ + (n - 2 + 2m)(2\epsilon_{\mathrm{CH}}{}^0 + \epsilon_{\mathrm{CC}}{}^0 - c/3) \\ + (a - b)\sum N_{CC}\Delta q_C + (4b - c)\sum \Delta q_{\mathrm{C}}\end{aligned} \tag{15}$$

Now, of course, it is possible to calculate the charges Δq_{C} along the lines which have been developed earlier[10-14] in a comprehensive way, using ab initio methods. More conveniently, however, one can use the relation[10,14]

$$\delta = -237.1(q_{\mathrm{C}} - 1)\ \mathrm{ppm} \tag{16}$$

between $^{13}\mathrm{C}$ nuclear magnetic resonance shifts, δ, relative to ethane and carbon net charges in the scale defined by setting the C net atomic charge of ethane = 1 arbitrary unit. The significance or generality of correlations like eq 16 is not known, and $^{13}\mathrm{C}$ shifts should not be indiscriminantly interpreted as being strictly linearly related to electron density in *all* systems. Now, this reservation should not obscure the fact that carbon charges in alkanes which are derived from chemical shifts are virtually in perfect agreement with their theoretical counterparts. Indeed, this equation has been found to be highly accurate for acyclic alkanes,[10] cyclohexane,[12] and six-membered polycyclic hydrocarbons.[13] Incidentally, the charges satisfying eq 16 are those corresponding to the "most even electron distribution", i.e., a situation whereby the various C atoms in alkanes are as similar as possible in charge.[10,15] This is relevant in connection with the approximation, eq 11.

Using now eq 16, $\Delta q_{\mathrm{C}} = -\delta/237.1$, and writing $\nu = 2\epsilon_{\mathrm{CH}}{}^0 + \epsilon_{\mathrm{CC}}{}^0 - c/3$, $\lambda_1 = (b - a)/237.1$, and $\lambda_2 = (c - 4b)/237.1$, eq 15 takes the form

$$\begin{aligned}\Delta E_{\mathrm{a}}^* = (1 - m)E_{\mathrm{a}}^*(\text{ethane}) \\ + (n - 2 + 2m)\nu + \lambda_1\sum N_{\mathrm{CC}}\delta + \lambda_2\sum\delta\end{aligned} \tag{17}$$

Table I. Molecular Energies (kcal/mol) and ^{13}C Shifts Used in the Comparison between Eq 7 and 17 for ΔE_a*

Molecule	$-\Delta H_f°$ (298.16 K, g)[a]	ZPE[f]	$H_T° - H_0°$[a]	ΔE_a*(exptl)	$\Sigma N_{CC}\delta$[i]	$\Sigma\delta$[i]	Deviation ($\Delta\Delta E_a$*) calcd − exptl
C_1	17.89	27.1[g]	2.40	419.24	0	−8	0.03
C_2	20.04[b]	45.16	2.86	710.54	0	0	0.00
C_3	25.02[b]	62.43	3.51	1004.07	39.8	29.6	0.27
C_4	30.03[b]	79.73	4.65	1298.15	91.0	52.8	−0.01
2-MeC_3	32.07[b]	79.61	4.28	1299.70	113.4	74.8	0.43
C_5	35.00	97.20	5.63	1592.20	139.6	77.6	−0.25
2-MeC_4	36.92	96.84[h]	5.30	1593.43	161.6	87.7	−0.18
2,2-Me_2C_3	40.27[c]	96.27	5.03	1595.94	190.4	124.4	0.34
C_6	39.96	114.37	6.62	1885.95	188.4	102.2	−0.19
2-MeC_5	41.66	(114.1)[h]	6.10	1886.86	208.9	114.2	0.25
3-MeC_5	41.02	(114.1)[h]	6.15	1886.27	209.5	101.1	0.11
2,2-Me_2C_4	44.35	113.60	5.91	1888.86	231.4	127.1	−0.28
2,3-Me_2C_4	42.49	113.73[h]	5.92	1887.14	222.8	110.0	0.18
C_7	44.89	131.67	7.62	2179.81	233.0[j]	124.3[j]	−0.52
2,2,3-Me_3C_4	48.96	130.61	6.70	2181.90	290.1[j]	145.7[j]	0.47
c-C_6	29.50[d]	103.30	4.24	1760.82	261.6[k]	130.8[k]	0.04
Me-c-C_6	36.99	120.50	5.23	2057.13	349.8[k]	169.7[k]	−0.37
1,1-Me_2-c-C_6	43.23	136.96	5.88	2351.11	396.0[k]	196.8[k]	−0.48
trans-Decalin	43.52[d]	160.68	6.22[f]	2815.50	630.8[l]	277.1[l]	0.06
Bicyclo[2.2.2]octane	23.75[e]	125.89[e]	4.94[e]	2218.40	363.7[m]	163.1[m]	0.34
Adamantane	30.65[e]	148.49	5.05[f]	2688.05	662.3[n]	285.4[n]	0.10

[a] Except as noted, experimental data are from F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", Carnegie Press, Pittsburgh, Pa., 1952. [b] D. A. Pittam and G. Pilcher, *J. Chem. Soc., Faraday Trans. 1,* **68,** 222L (1972). [c] G. Pilcher and J. D. M. Chadwick, *Trans. Faraday Soc.,* **63,** 2357 (1967). [d] J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970. [e] R. H. Boyd, S. N. Sanwal, S. Chary-Tehrany, and D. McNally, *J. Phys. Chem.,* **75,** 1264 (1971). [f] Data based on experimental and calculated frequencies from R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta,* **21,** 169 (1965). [g] T. L. Cottrell, *J. Chem. Soc.,* 1448 (1948). [h] S. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.,* **92,** 3109 (1970). [i] D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.,* **86,** 2984 (1964). [j] L. P. Lindeman and J. A. Adams, *Anal. Chem.,* **43,** 1245 (1971). [k] J. D. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972. [l] K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.,* **95,** 3718 (1973). [m] G. E. Maciel and H. C. Dorn, *J. Am. Chem. Soc.,* **93,** 1268 (1971). [n] G. E. Maciel, H. C. Dorn, R. L. Green, W. A. Kleschick, M. R. Peterson, and G. H. Wahl, *J. Org. Magn. Reson.,* **6,** 178 (1974).

which enables the calculation of the ΔE_a*'s from ^{13}C NMR shifts only and is suitable for comparisons with experimental ΔE_a* values. Solving eq 17 for methane, one obtains $\Delta E_a^*(CH_4) = \Delta E_a^*(C_2H_6) - \nu + \lambda_2\delta(CH_4)$ and, therefrom,

$$\begin{aligned}\Delta E_a^* = {} & (1-m)\Delta E_a^*(C_2H_6) \\ & + (n-2+2m)[\Delta E_a^*(C_2H_6) - \Delta E_a^*(CH_4)] \\ & + \lambda_1\textstyle\sum N_{CC}\delta + \lambda_2[(n-2+2m)\delta(CH_4) + \sum\delta] \qquad (18)\end{aligned}$$

which separates the purely additive contributions from the charge dependent ones.

Results and Discussion

The experimental ΔE_a* values, as well as the enthalpies of formation (at 25 °C), the zero-point energies, and the thermal terms which were used in eq 7 for deriving them, are indicated in Table I. The comparison of eq 17 with these experimental ΔE_a* results yields $\nu = 290.814$, $\lambda_1 = 0.03244$, and $\lambda_2 = 0.05728$ kcal/mol. Of course, not too much importance should be attached to the exact values of these parameters, as they may slightly change in the future with the use of additional and more precise experimental data. The chemical shifts relative to ethane, δ, were calculated using NMR results extracted from literature. The deviations which are reported represent the difference, ΔE_a*(calcd) − ΔE_a*(exptl), between the ΔE_a* values calculated from eq 17, using ^{13}C NMR shifts, and their experimental counterparts. Equation 18 yields, of course, the same results, with $\Delta E_a^*(C_2H_6) - \Delta E_a^*(CH_4) = 291.27$ kcal/mol.

The mean deviation (0.23 kcal/mol) is satisfactory considering the simplicity of eq 17 (or eq 18) which, admittedly, represents the crudest possible approach in terms of charges. While it remains possible that some of the individual deviations point at the necessity for a more sophisticated treatment, it should be considered that any attempt directed toward better numerical agreements should be preceded by an examination of the experimental data. These deviations collect, indeed, possible experimental errors from four sources, including possible errors in calibration of the NMR results.[16]

The present two parameter (λ_1,λ_2) scheme compares favorably in quality, and because it includes "strain-free" cyclic compounds with any other additivity scheme. The difficulties associated with the evaluation of ring strain and with the selection of an appropriate strain-free reference compound have been discussed in some detail by Schleyer;[17] these difficulties are ignored in the present study since ring strain (e.g., in adamantane), even if real, does not affect[13] the relationship (eq 16) between atomic charges and the ^{13}C shifts which are used in eq 17 and 18. The quality of numerous bond additivity schemes has been reviewed by Cox and Pilcher.[18] Only heavy empirical parameterization (typically 7 or more parameters) yields results for *acyclic* alkanes which can be compared in quality with our results. The most successful additivity method, that proposed by Allen et al.,[4] demonstrated on empirical grounds a requirement for seven parameters; then the heats of formation of all saturated acyclic hydrocarbons with eight carbon atoms or less are correlated with an average deviation of ±0.30 kcal/mol.[19]

Considering the results given in Table I we may thus regard that, at this stage, any further numerical improvement is illusory. Indeed, if quadratic terms in the Taylor expansion (eq 12) or specific steric effects which were hitherto neglected were to be taken into consideration, the accompanying proliferation of parameters would help in reducing the deviations without adding, however, anything substantial to the understanding of the basic phenomena which are involved. Present results support our analysis of the molecular energy in terms of bond contributions and the view that the latter can be adequately approximated by a linear combination of the charges of the

Table II. Comparison between Experimental and Calculated Values for ZPE and ZPE + E_{vib} Using Addivity Rules (kcal/mol)

Molecule	ZPE (calcd) − ZPE(exptl)			Deviation in (ZPE + E_{vib})	
	a	*b*	ZPE + E_{vib}	*c*	*d*
C_1	0.67	−0.04	27.13	0.59	−0.66
C_2	0.00	0.00	45.65	0.00	0.00
C_3	0.08	0.17	63.57	0.44	0.36
C_4	−0.11	0.09	82.01	−0.48	0.02
2-MeC_3	0.15	−0.14	81.52	1.02	−0.06
C_5	−0.41	−0.10	100.46	−1.21	−0.30
2-MeC_4	−0.11	−0.11	99.77	−0.42	−0.09
2,2-Me_2C_3	0.79	0.03	98.93	2.36	−0.03
C_6	−0.42	0.00	118.62	−1.67	−0.32
2-MeC_5	−0.16	−0.07	117.83	−0.59	0.00
3-MeC_5	−0.39	−0.11	117.88	−1.67	0.01
2,2-Me_2C_4	0.33	0.06	117.14	0.40	−0.08
2,3-Me_2C_4	−0.01	0.04	117.28	−0.80	0.30
C_7	−0.55	0.03	136.92	−2.34	−0.39
2,2,3-Me_3C_4	0.27	0.13	134.94	−0.47	0.35
c-C_6	−0.28	(0.83)	105.17	0.69	(4.34)
Me-c-C_6	−0.48	(0.23)	123.36	0.08	(4.49)
1,1-Me_2-c-C_6	0.29	(1.09)	140.47	0.94	(4.50)
trans-Decalin	−0.66	(0.55)	164.53	−0.60	(6.65)
Bicyclo[2.2.2]octane	0.47	(3.67)	128.46	0.32	(10.13)
Adamantane	0.69	(3.20)	151.17	1.39	(12.15)

[a] Calculated from ZPE = $45.16(1 - m) + 17.255(n - 2 + 2m) - 0.0105\Sigma N_{CC}\delta + 0.072\Sigma\delta$, including cyclic compounds. [b] Calculated from ZPE = $45.16(1 - m) + 18.082(n - 2 + 2m) - 0.0178\Sigma N_{CC}\delta + 0.0021\Sigma\delta$, excluding the cyclic compounds. [c] Calculated from ZPE + $E_{\text{vib}} = 45.65(1 - m) + 17.310(n - 2 + 2m) - 0.0310\Sigma N_{CC}\delta + 0.0773\Sigma\delta$, for all compounds. [d] Calculated from ZPE + $E_{\text{vib}} = 45.65(1 - m) + 19.226(n - 2 + 2m) - 0.0195\Sigma N_{CC}\delta - 0.0057\Sigma\delta$, for acyclic hydrocarbons. The numbers in parentheses are calculated using the equations in footnotes *b* and *d*, respectively, which were obtained for the acyclic hydrocarbons.

bond-forming atoms. Moreover, it is clear that at no time has there been any need for introducing corrections which might go under the heading "ring strain", thus differentiating our approach from other bond-energy schemes which fail whenever used for the estimation of heat-of-formation data of cyclic structures if they do not include strain-energy terms.

Some insight into this latter aspect follows from the analysis of zero-point and thermal energies in terms of bond additivity schemes. We examine here whether these quantities obey, on an empirical basis, expressions having the same structure as eq 17. The best possible correlation (Table II, footnote *a*) for the ZPE's disqualifies itself if cyclic compounds are included (average deviation = 0.35 kcal/mol) but is quite acceptable (Table II, footnote *b*) if derived only for the acyclic hydrocarbons (average deviation = 0.075 kcal/mol). Similarly, the correlation fails for the sum ZPE + E_{vib} (Table II, footnote *c*) if cyclic compounds are included but appears to be a satisfactory empirical approximation (except for CH_4) if limited to the open-chain hydrocarbons (Table II, footnote *d*), with an average deviation of 0.20 kcal/mol.

These results cover several of Cottrell's arguments,[20] i.e., that zero-point energy would be, in hydrocarbons at least, very approximately an additive bond property, whereas the heat content is not likely to be additive but depends on the shape of the molecule. Care must therefore be exerted in applying the correlation (Table II, footnote *d*), e.g., to highly branched alkanes. It remains, however, that the quality of this correlation now explains the success of our earlier bond-energy scheme[6] for acyclic alkanes, constructed from the hypothesis ΔH(atomization) = $\Sigma\epsilon_{ij}$, with ϵ_{ij}'s expressed in terms of charges. Indeed, the success of such an approach implies that both $\Delta E_a{}^*$ and (ZPE + E_{vib}) obey expressions like eq 17.

In conclusion, present results indicate that bond-additivity schemes involving enthalpies of atomization at 25 °C cannot be applicable to cyclic compounds, unless introducing empirical correction terms. The energy of atomization at the hypothetical vibrationless state appears to be the only quantity which can be truly apportioned among bonds, with equal success for six-membered cyclic compounds as for the acyclic hydrocarbons.

Table III. Increments of ZPE + $H_T - H_0$ for CH_2 Groups in Linear Paraffins (kcal/mol)

	C_{n+1}-C_n	C_{n+2}-C_n	C_{n+3}-C_n	C_{n+4}-C_n
$n = 1$	18.52	36.44	54.88	73.33
$n = 2$	17.92	36.36	54.81	72.97
$n = 3$	18.44	36.89	55.05	73.35
$n = 4$	18.45	36.61	54.91	
Av	18.33	36.58	54.91	73.22
Av for CH_2	18.33	18.29	18.30	18.31

Additional Verifications. The molecules used for testing our bond energy scheme (Table I) represent all those of this class of compounds for which the set of the required experimental results is complete. Their number is limited, primarily because of the scarcity of vibrational spectral data. We now wish to illustrate the predictive ability of our scheme in selected cases where ZPE and $H_T - H_0$ energies are not known from experiment.

If $\Delta H_f°$'s are to be calculated, the success of such an endeavor rests upon the possibility of estimating the required ZPE + $H_T - H_0$ values in a simple manner. The following empirical approach is based upon the results of Table I for acyclic alkanes, which obey an approximate additivity rule illustrated in Table III. The results displayed therein are the differences in the sum ZPE + $H_T - H_0$ between the C_{n+1} and C_n hydrocarbons and represent the increments for one added CH_2 group, between the C_{n+2} and C_n hydrocarbons (for two CH_2 groups), etc. The average increment of the ZPE + $H_T - H_0$ contributions is then 18.31 ± 0.14 kcal/mol for one linear paraffinic CH_2 group.

Using this increment, ethyl- and *n*-butylcyclohexane are calculated from methylcyclohexane (Table IV). The increment for one equatorial methyl group (18.19) is estimated from methylcyclohexane and cyclohexane and is used for di- and trimethyl derivatives (**3**, **5**, **7**, **9**, **12**, **14**) with all groups in

Table IV. Alkyl-Substituted Cyclohexanes and Selected Polycyclic Compounds

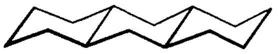
Molecule[a]	$\Sigma N_{CC}\delta$[b]	$\Sigma\delta$	ΔE_a*	$ZPE + H_T - H_0$[c] Model	$ZPE + H_T - H_0$[c] "Exptl"	$\Delta H_f°$ Calcd	$\Delta H_f°$ Exptl[d]
1 ethyl	402.1	186.8	2350.26	144.0	144.2	−41.22	−41.05 ± 0.37
2 *n*-butyl	492.1	234.3	2937.52	180.7	180.3	−50.52	−50.92 ± 0.33
3 1,2-Me_2 trans	444.5	202.9	2352.55	143.9	144.5	−43.61	−43.00 ± 0.45
4 1,2-Me_2 cis	374.0	168.3	2348.28	142.0	142.1	−41.24	−41.13 ± 0.44
5 1,3-Me_2 cis	441.5	210.8	2352.91	143.9	143.7	−43.97	−44.13 ± 0.42
6 1,3-Me_2 trans	378.6	182.4	2349.24	142.0	142.0	−42.20	−42.20 ± 0.40
7 1,4-Me_2 trans	441.3	210.7	2352.90	143.9	143.7	−43.96	−44.12 ± 0.40
8 1,4-Me_2 cis	387.3	177.6	2349.25	142.0	142.0	−42.21	−42.22 ± 0.40
9 1-cis-3-cis-5	532.4	251.4	2649.00	162.1	162.6	−51.03	−51.48
10 1-cis-3-trans-5	462.6	223.1	2645.11	160.2	160.1	−49.24	−49.37
11 1-trans-2-trans-3	452.5	197.7	2643.33	160.2		−47.46	
12 1-trans-2-cis-3	529.9	231.7	2647.79	162.1		−49.82	
13 1-cis-2-cis-3	452.7	192.0	2643.01	160.2		−47.14	
14 1-trans-2-trans-4	529.0	240.6	2648.27	162.1		−50.30	
15 1-trans-2-cis-4	464.1	211.5	2644.50	160.2		−48.63	
16 1-cis-2-trans-4-	451.7	205.7	2643.76	160.2		−47.89	
17 1-cis-2-cis-4	458.0	205.4	2643.95	160.2		−48.08	
18 *cis*-decalin	539.8	238.2	2810.38	165.0	164.9	−40.30	−40.43 ± 0.56
19 spiro[5.5]undecane	576.3	261.3	3103.70	183.2	183.2	−44.79	−44.81 ± 0.75
20 TST	997.4	422.9	3870.15	226.2	225.6	−57.57	−58.13 ± 1.39
21 TAT	900.5	389.2	3865.08	226.9	226.0	−52.50	−52.74 ± 1.47
22 diadamantane	1090.3	427.2	3615.59	199.5	199.1	−32.15	−32.60 ± 0.58

[a] **1–17** are substituted cyclohexanes. TST and TAT are the *trans-syn-trans-* and *trans-anti-trans*-perhydroanthracenes. [b] Calculated from ^{13}C shifts reported by J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972 (**1–10, 12, 14, 15**). D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **94**, 5318 (1972) (**11, 13, 16, 17**). D. K. Dalling and D. M. Grant, *J. Am. Chem. Soc.*, **96**, 1827 (1974) (**20, 21**). T. M. Gund, E. Osawa, V. Z. Williams, and P. v. R. Schleyer, *J. Org. Chem.*, **39**, 2979 (1974) (**22**). D. K. Dalling, D. M. Grant, and E. G. Paul, *J. Am. Chem. Soc.*, **95**, 3718 (1973) (**18, 19**). [c] As described in the text, for **1–17**. The comparisons involving molecules **3–10** indicate consistently a lowering of ~1.9 kcal/mol in the $ZPE + H_T - H_0$ term each time a C atom is found in axial rather than in equatorial position with respect to a cyclohexane ring. The same effect is assumed in the estimate of *cis*-decalin, with respect to its trans isomer, and for spiro[5.5]undecane, an isomer of methyldecalin, which is estimated by adding the 18.19-kcal/mol increment to the value estimated for *cis*-decalin. For compounds **20** and **21**, the group increment added to the value for *trans*-decalin (166.9) is the difference between *trans*-decalin and cyclohexane. Similarly, the increment added to adamantane to give **22** is the difference between adamantane and cyclohexane. The "experimental" values are obtained from a back-calculation, using eq 7. [d] Extracted from J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, New York, N.Y., 1970 (**1–8, 18, 20, 21**). C. J. Egan and W. C. Buss, *J. Phys. Chem.*, **63**, 1887 (1959) (**9, 10**). T. Clark, T. McO. Knox, H. Mackle, A. McKervey, and J. J. Rooney, *J. Am. Chem. Soc.*, **97**, 3835 (1975) (**22**). D. J. Subach and B. Zwolinski, *J. Chem. Eng. Data*, **20**, 232 (1975) (**19**).

equatorial position. The axial–equatorial situation is simulated assuming the $ZPE + H_T - H_0$ value (142.0) of *cis*-1,4-dimethylcyclohexane, calculated from ΔE_a* and $\Delta H_f°$ using eq 7. The $\Delta H_f°$'s calculated from these estimates and from the ΔE_a*'s derived from ^{13}C shifts (eq 17) compare favorably with their experimental counterparts (Table IV), with an average deviation of 0.22 kcal/mol over a range of ~10 kcal/mol.

These results also indicate that trimethylcyclohexane isomers differing by the conformational position of one methyl group (i.e., **9** vs. **10**, **11** vs. **12**, **12** vs. **13**, **14** vs. **15**, **14** vs. **16**, and **14** vs. **17**) exhibit average energy and enthalpy differences of 4.2 and 2.3 kcal/mol, respectively. For dimethylcyclohexanes (**3** vs. **4**, **5** vs. **6**, and **7** vs. **8**), the corresponding figures are 3.9 and 1.9 kcal/mol. The average stabilization of the equatorial vs. the axial form of 1.9–2.3 kcal/mol (enthalpy, at 25 °C) calculated from our scheme is reasonably close to the currently accepted value of ~1.8 kcal/mol, which itself is not an observed quantity but an estimate extrapolated from, and consistent with, numerous data collected from other molecules. In conclusion, our scheme reproduces both the essential features of conformational analysis and the detailed differences between isomers (**3** vs. **5** vs. **7** and **4** vs. **6** vs. **8**), a result which depends solely upon the charge-depending part $\lambda_1\Sigma N_{CC}\delta + \lambda_2\Sigma\delta$ of eq 17 and 18. In that respect, the result obtained for diadamantane (**22**) is impressive, considering the large weight of the charge-dependent part, 49.8 kcal/mol (eq 18).

The low-temperature ^{13}C shifts of the C-3, C-5, and methyl carbon atoms of axial methylcyclohexane are ~6 ppm upfield from those of the equatorial form,[21] thus decreasing $\Sigma N_{CC}\delta$ and $\Sigma\delta$ by 30 and 18 ppm. The ΔE_a* energy of the axial form is then (eq 17) $30\lambda_1 + 18\lambda_2 = 2.00$ kcal/mol lower than that of the equatorial conformer. For the boat form of cyclohexane, we have calculated δ 16.4 for carbons 1 and 4 and δ 22.2 (from TMS) for the other four C atoms, using Grant's parameters.[22] Then, $\Sigma N_{CC}\delta$ and $\Sigma\delta$ are lowered by 89.2 and 44.6 ppm with respect to cyclohexane (δ 27.7), thus showing that the boat form is $89.2\lambda_1 + 44.6\lambda_2 = 5.45$ kcal/mol less stable than the chair form. This result agrees with the measured energy increment (5.39 kcal/mol) between the *trans-anti-trans-* (**21**) and *trans-syn-trans-* (**20**) perhydroanthracenes, which differ only because of the center boat in the TAT compound, and with the difference in ΔE_a*, 5.07 kcal/mol, calculated from their



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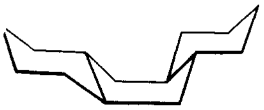

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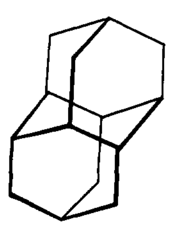

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^{13}C spectra (Table IV). We can now estimate the relative energies of the various forms of butane. Taking the boat and chair forms of cyclohexane as models, we assume a similar pattern in ^{13}C shifts for eclipsed and gauche butane as in the model compounds, i.e., a decrease of 11.3 and 5.5 ppm for the terminal and central C atoms of eclipsed butane. The latter is thus $44.6\lambda_1 + 33.6\lambda_2 = 3.37$ kcal/mol less stable than gauche butane. Similarly, taking axial and equatorial methylcyclohexane as models for the gauche and anti forms of butane, the 6 ppm upfield shift of the C-3, C-5, and CH_3 carbons observed for the axial conformer results in a destabilization of $12\lambda_1 + 12\lambda_2 = 1.08$ kcal/mol of gauche butane with respect to its anti form. These conformational results, which are entirely derived from ^{13}C shifts, are in general agreement with currently accepted values, moreover as for these structures the variations in zero-point and thermal energies represent, in all likelihood, only minor contributions.[23]

While the examples presented here illustrate that reasonably reliable binding energies are easy to derive from ^{13}C spectral data, it also appears that in any calculation of an enthalpy of formation the real problem is now one of estimating the vibrational contributions in a simple manner. The ΔE_a^* energies represent nonetheless valuable information in problems of molecular stability. Since ^{13}C shifts are farther downfield as carbon atoms are closer to electroneutrality and both λ_1 and λ_2 are positive quantities, we can express the overall conclusion as a thumb rule: "in comparisons between isomers, the more stable compound is that whose carbon skeleton best approaches electroneutrality, which is reflected by larger (downfield) δ values".

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(15) In the scale defined by q_C(ethane) = 1 arbitrary unit, the carbon net charges range[14] from 1.031 (methane) to 0.862 (C_{sec} in adamantane), all carbons being positive.
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Volumes and Heat Capacities of Ternary Aqueous Systems at 25 °C. Mixtures of Urea, *tert*-Butyl Alcohol, Dimethylformamide, and Water

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Abstract: The densities and heat capacities per unit volume were measured for the systems urea (U)-*tert*-butyl alcohol (TBA)-water (W) and dimethylformamide (DMF)-TBA-W at 25 °C with a flow densimeter and a flow microcalorimeter. One of the nonaqueous components was kept at a constant low concentration and whenever possible the other component was varied over the whole mole fraction range. From these data, combined with previously published data on NaCl-U-W and on Bu_4NBr-U-W, volumes and heat capacities of transfer were calculated and compared with the corresponding excess functions of the binary systems to get an overall view of these ternary systems. In the water-rich region the thermodynamic properties are characterized by strong solute-W and solute-solute interactions. At the nonaqueous end the thermodynamic properties are reflecting mostly solute-solvent interactions. Through an understanding of the two ends it becomes easier to account for the various inflection points, maxima or minima in the transfer functions.

Mixed aqueous solvents are used intensively in chemistry, biology, and industry to control factors such as solubility, stability of systems, and kinetics of reactions. Despite numerous studies on thermodynamic, transport, and spectral properties,[2a] there is still disagreement on the nature of the interactions which are responsible for the characteristic trends in the composition dependence. For example, often maxima, minima, or inflection points are observed which are then interpreted in terms of various effects such as structural changes in the solvent, preferential hydration, or association complexes. However, depending on the property studied, these extrema or inflection points often do not occur at the same mole fraction and depend on the nature of the solute, making many of these interpretations dubious.

Much of the confusion probably comes from the limited range of most studies. A better understanding of ternary