Bond Energy/Group Contribution Methods of Calculating the Standard Heat of Formation: Development of a New Generalized Bond-Energy Scheme for Monomers and Polymers. Part II. Hydrocarbons

R. M. Joshi[a]

[a] National Chemical Laboratory, Poona, India

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R. M. JOSHI

National Chemical Laboratory
Poona 8, India

SUMMARY

A new bond-energy scheme is developed for calculating the heats of formation (ideal gas, 298°K, 1 atm) of alkenes, alkadienes, alkynes, and aromatic hydrocarbons, in continuation of the earlier part of the scheme for alkanes. The over-all precision is about ±0.5 kcal/mole and the scheme is easily applicable to polymers. Both the C–H and C–C bond-energy terms fulfill a linear relationship in respect of the bond strength vs. the bond length, for which least-square equations have been derived. A few other earlier bond energy/group contribution methods are compared with the present scheme, treating all available experimental data reported in literature on about 200 hydrocarbons including 10 polymers.

INTRODUCTION

In Part I of this series [*J. Macromol. Sci.–Chem.*, **A4**, 1819-1839].

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*N.C.L. Communication No. 1502.

(1970)] experimental heats of formation (ideal gas, 298°K, 1 atm) of 70 alkanes, including a few α-olefin polymers, were fitted in within a standard error of 0.28 to 0.31 kcal/mole, using the new bond-energy terms taken from a general scheme for organic compounds (monomers and polymers) under development. Accurate prediction of the heat of formation (the most important and primary thermodynamic quantity), in respect of a vast array of polymers now becoming available through the incessant efforts of polymer chemists for new materials over the past two decades, has been one object of this work. The existing experimental data on monomers and polymers is yet quite meagre as observed in a recent review [1] some 10 years after the pioneering work of Dainton and Ivin [2].

Although the experimental precision attained in modern bomb calorimetry is sufficiently high (±0.01 to 0.02%), combustion measurements on polymers present a few basic difficulties. First, the purity: low molecular weight organic compounds are at least of "three-nine" (99.9%) purity as the minimum accepted thermochemical standard, rather fairly easily attained by usual methods such as repetitive crystallizations, fractional distillations, or sublimations, but none applicable to polymers. More advanced methods [3], such as zone refining and the new "freezing staircase" technique of the U.S. National Bureau of Standards, developed by Saylor [4] claiming an "absolute" moleculewise purity, may not also easily apply to polymers. The inevitable presence of foreign end-groups in a polymer prepared through the usual methods of free-radical, ionic, or Ziegler initiation is also an additional "impurity" in the thermochemical sense, precluding the attainment of purity beyond 99.9% even theoretically in a polymer of 1000 DP. However, if the end groups are known with certainty as in a well characterized polymer, a correction can be worked out without much detriment to the high precision of the combustion calorimetry. A more serious difficulty in the experimental work on polymers arises from the indefinite physical state of the polymer in the "condensed solid" form, designated as (c) in the earlier work [2]. A fully crystalline solid state (c″), ideally a single crystal, is only attainable in a few hydrocarbon polymers, particularly polyethylene on which some thermodynamic properties measurements have been reported recently [5]. In general, the (c)-state polymer at room temperature (20-30°C range of the bomb calorimetry) comprises, in terms of physical definitions, the fully crystalline region/portion + the amorphous polymer existing in either the liquidlike (plastic or rubbery) state, or the glassy state, or partly both. The energy contribution due to the partial crystallinity in a polymer sample

taken for combustion can be explicitly determined by actual auxiliary calorimetric work of measuring the heat of fusion, or by calculation from the known crystallinity (determined through x ray and other methods) and the molar heat of fusion evaluated by Flory's well-known method of melting point depression [6]. But assessment of the energy "frozen" in the glassy state of a polymer, especially when its glass-transition temperature is several tens of degrees above the room temperature, is more difficult, requiring many auxiliary calorimetric measurements of the heat of solution of identical polymer in a θ-solvent, or the specific heats of glassy and liquid states. The question arises as to what should be the ideal state of the polymer for comparison of its heat of formation to correlate bond energies, steric hindrance, resonance, etc., with structure. A totally amorphous, liquidlike (rubbery, in case of elastomers) state above the glass-transition temperature appears to be the right choice for comparison of polymers among themselves. Some of the earlier data on heats of polymerization/formation and inferences about steric hindrance thus need a revision, particularly for those polymers that exist in the glassy state at room temperature. Since the glass-transition temperatures of most of the α-olefin polymers are below 25°C, the recent combustion data on these polymers [7], where the energy of partial crystallization was additionally measured, are of value for correlation of the steric hindrance, flexibility of chain, bond energies, and other physical properties of different structures [8]. On the contrary, gross combustion data of general precision on many nonspecific industrial polymers reported recently [9] has much less significance to the thermochemist. The development of a good bond-energy scheme instead, can save a lot of such experimental work and labor on many hundreds of industrial polymers yet unstudied.

There is yet another reason for preferring a good bond-energy scheme to the experimental (combustion) work on polymers. Although reducing the heat of formation data to the liquid state should suffice for the purpose of comparison and correlation within the polymers, it is always necessary to transform the data to the ideal gas state if a correlation is sought with small molecules, the monomers, for understanding the polymerization equilibrium and the high-temperature reactions of polymers such as ablation. The ideal gas state for a long chain polymer is obviously "hypothetical" and so is the quantity: heat of vaporization, which cannot be measured by any experimental technique. Any highly precise experimental combustion data on polymers (in the ideal liquidlike state) would ultimately have to be combined with the hypothetical heat of vaporization estimated only through empirical correlation and group contribution principles. The development of

such precise schemes for prediction of both the heat of formation and the heat of vaporization (in the first instance at 298°K) has been the general object of the work reported in this and subsequent papers. In this process a comprehensive survey of the experimental thermochemical data is made and selected data employed for deriving the new bond-energy and group-contribution terms. Heats of formation on many polymer structures are predicted and compared with observed data on some polymers. The present paper deals with hydrocarbons and hydrocarbon polymers.

DERIVATION OF BOND-ENERGY TERMS AND ABSOLUTE BOND ENERGIES

Nomenclature

(1) The state of hybridization of an atom is shown by a numerical superscript, for example: C^1, sp (diagonal symmetry); C^2, sp^2 (trigonal); C^3, sp^3 (tetrahedral); C^ϕ, an aromatic carbon with hexagonal symmetry; C^0, an allene type of sp^2 symmetry, etc.

(2) The type of bond between two atoms is shown by the usual dash line joining them, viz., C^3-C^3, a single bond between two tetrahedral carbons; $C^2=C^2$, a double bond; C^2-C^2, a single bond between two sp^2 carbon atoms, etc. An aromatic bond is shown by $\because$, and a van der Waals-type repulsive interaction or a hydrogen-bonding interaction by •••••.

(3) The superscripted primes, such as H', H'', and H''' on a univalent atom such as hydrogen or halogen, or on a group such as the phenyl, e.g., ϕ'', mean the number of such atoms or groups together present on the bonded partner in the molecule. The bond energy term here applies to each bond of this type; for example, C^3-H''' is one of the three carbon-hydrogen bonds in a methyl group each contributing -3.48 kcal/mole (see Table 1) to the heat of formation; similarly, C^2-H' is a carbon-hydrogen bond in propylene, with -5.68 kcal as the energy term.

(4) For alkanes <u>only</u> (or for an alkanetype side chain in a compound), a carbon atom placed in parenthesis indicates that the atom is third or higher from the nearest chain-end of the longest chain. A parenthesis superscripted with a star ( )* shows a deeply embedded carbon atom with its position third or deeper in the molecule from any end of the longest chain (see Part I).

(5) The numerical subscript (in small numerals) on the symbol letter

of an atom indicates the total number of its bondages <u>with carbon atoms</u> in a molecule. Thus C_1^3 is a primary carbon as in $-CH_3$, C_3^3 a tertiary as in $\geqq CH$, C_2^2 meaning $=CH$, and so on. A star as a subscript, C_*, denotes a carbon atom without any hydrogen in an infinite network; for example, C_*^3 in the diamond lattice, C_*^ϕ in graphite, and C_*^0 in polyallene or "carbene" polymer. A C_*^ϕ is also the bridging carbon atom in fused aromatic rings. A subscript in lower case letters placed on the atom in parenthesis denotes any other association of the atom influencing the bond for which the bond energy term stands; viz., $(C^3)_{co}$ and $(C^2)_0$ indicate the carbon atoms already connected to a carbonyl group as in a ketone, or to an etheral oxygen, respectively. These kinds of symbols will be used in future parts of the scheme to be published. A numerical subscript is omitted where it is not significant.

(6) Terms in square brackets indicate the steric interaction (with a + sign) causing higher internal energy of the molecule with strained bonds. Terms placed in large, bold-face parenthesis denote the conjugation energy (with a – sign) due to the effects of delocalization lowering of the over-all energy of the molecule. Both these kinds of terms cannot be ascribed to any particular bond in the molecule but relate to the entire group of atoms (placed in square bracket or parenthesis) constituting the structural feature responsible for the energy contribution.

(7) Some bond energy <u>values</u> placed in parenthesis in Table 1, are "special-purpose" terms to be employed for (and are derived from) the data on alkanes and alkenes only, or to long side chains of the type. In order for cyclohydrocarbons, halocarbons, oxygen- and nitrogen compounds, etc., to follow this system in future parts of this scheme, none of the special terms have been used to derive further bond energies of the new related bonds. The corresponding absolute bond energies of the special terms thus have no real significance as they arise only as a result of the nonbonded hydrogens interactions in some alkanes and alkenes being ascribed to the particular special bond. Such special terms have been underlined in column 5 of the Table 1.

General Procedure

The experimental thermochemical data on heats of formation of hydrocarbons have been surveyed up to the middle of 1970 and are compiled in Column 3 of the Tables 2 to 5. The heat of formation in the ideal gas phase is derived, as far as possible, by using experimental values of the

Table 1. Bond-Energy Terms and Steric and Resonance-Energy Corrections; Absolute Bond Energies and Bond Lengths

No.	Bond/group	Compounds (from which derived)[a]	Energy term ΔH_f° (g) (kcal/mole)	Bond energy E° (298°K)[b] (kcal/mole)	Bond length[c] L (Å)
(1)	(2)	(3)	(4)	(5)	(6)
		Carbon-Hydrogen Bonds			
1	C^3–H'	Basic energy terms taken	-1.78 ± 0.10	96.7	1.094 ± 0.002
2	C^3–H''	from the Cox scheme [11]	-2.68 ± 0.12	97.6	
3	C^3–H'''	based on the original work	-3.48 ± 0.14	98.4	
4	C^2–H'	of Dewar and Schmeising	-5.68 ± 0.20	100.6	
5	C^2–H''	[10]	-6.38 ± 0.20	101.3	1.085 ± 0.002
6	$C\phi$......H	4 (2,5,14,20,21,25,26)	-6.80 ± 0.30	101.7	1.084
7	C^1–H	2 (11,12)	-15.75 ± 0.15	110.7	1.059
		Carbon-Carbon Single Bonds			
	C^3–C^3 bonds				
8	C^3_*–C^3_*	5 (8); diamond lattice	0.23	85.4	1.545
9	C^3_1–C^3	Basic energy term taken from	0.45 ± 0.05	85.2	1.54 ± 0.005
	C^3_2–C^3_2	the Cox scheme [11]			
	C^3_3–C^3_2				

Table 1. (continued)

(1)	(2)	(3)	(4)	(5)	(6)
22	C^2_2–C^3_3	2 (11,19,24-25)	-4.92 ± 0.13	90.6	
23	C^2_2–C^3_4	2 (28,41,46,52)	-3.30 ± 0.34	88.9	
24	C^3_3–C^1_3	2 (6,10,18,26)	-4.15 ± 0.23	89.8	
	C^3_3–C^2_3				
	C^3_3–C^2_2				
25	C^2_3–C^3_3	2 (24,47)	-4.42 ± 0.31	90.1	
26	C^3_3–C^3_4	2 (43)	-1.35	87.0	
27	$C\phi$–C^3_3	4 (2,3,7,8,11-12,15,17,27)	-4.24 ± 0.23	89.9	
28	$C\phi$–C^3_4	4 (18,23,24)	-2.05 ± 0.25	86.6	1.505 ± 0.005
	C^2–C^2, C^2–$C\phi$ and $C\phi$–$C\phi$ single bonds.				
29	C^2–C^2	3 (3,6,10)	-12.97 ± 0.15	98.6	1.483
30	C^2–$C\phi$	4 (30,32,34,35,36)	-10.75 ± 0.21	96.4	
31	$C\phi$–$C\phi$	4 (42)	-10.75	96.4	1.492
	C^1–C^3, C^1–C^2, C^1–$C\phi$ and C^1–C^1 single bonds				
32	C^1–C^1	3 (12,13,15)	-15.09 ± 0.14	100.7	1.459
33	C^1–C^3	3 (17)	-15.59	101.2	
	C^1–C^2				

No.	Bond	Source			
10	$(C^3)-C^2$	Derived from 6 hydrocarbons,	(0.77 ± 0.11)	84.9	
	$(C^3)*-C^2$	See Part I			
11	C^3-C^3	Part I	1.03	84.6	
12	C^4-C^2	Part I (4 hydrocarbons)	1.12 ± 0.19	84.5	
13	$(C^4)-C^2$	Part I (4 hydrocarbons)	1.47 ± 0.28	84.2	
	$(C^4)*-C^2$				
14	$(C^3)-C^3$	Part I (4 alkanes)	(1.86 ± 0.05)	83.8	
	$(C^3)-(C^3)$				
15	$(C^3)*-C^3$	Part I (2 alkanes)	(2.60 ± 0.38)	83.0	
16	C^4-C^3	Part I	2.77	82.9	
17	$C^4-(C^3)$				
	$(C^4)-C^3$	Part I (7 alkanes)	(3.56 ± 0.28)	82.1	
	$(C^4)-(C^3)$				
18	$C^4-(C^3)*$	Part I	(5.78)	79.9	
19	C^4-C^4	Part I (2 alkanes)	6.54 ± 0.6	79.1	
	$(C^4)-C^4$				

C^2-C^3 and $C\phi-C^3$ bonds

No.	Bond	Source			
20	C^2-C^3	2 (2,5)	-4.22 ± 0.02	89.9	1.510 ± 0.005
21	C^2-C^2	2 (3,7,8-9,13,15,16-17, 30-31,32-33,34,44,50)	-4.40 ± 0.23	90.0	1.510 ± 0.005

	Bond	Reference			
34	C^1-C^2	3 (19,22)	-21.60 ± 0.11	107.2	1.439 ± 0.010
35	C^1-C^ϕ	3 (Z4j)	-18.83	104.5	1.450
36	C^1-C^1	3 (23,28)	-36.83 ± 0.02	122.5	1.371 ± 0.005

$C^\phi\cdots C^\phi$, $C^2=C^2$, $C^0=C^2$, $C^0=C^0$ and C^1-C^1 higher-order bonds

	Bond	Reference			
37	$C^\phi\cdots C^\phi$	4 (1); basic term	10.10	118.4	1.394 ± 0.005
38	$C^\phi_*\cdots C^\phi$		7.03 ± 0.10	114.3	
39	$C^\phi_*\cdots C^\phi_*$	4 (43,45,47,48)	1.53 ± 0.16	112.7	1.421 graphite lattice
40	$C^2_1=C^2$	2 (1); basic term	38.00	133.3	1.340 ± 0.020
41	$C^2_2=C^2_3$	2 (12,21,22-23,35-36,39,49)	(39.00 ± 0.32)	132.3	
42	$C^2_3=C^2_3$	2 (29)	(39.82)	131.5	
43	$C^0=C^2$	3 (1,2,4,8)	35.95 ± 0.37	135.3	1.310
44	$C^0=C^2_3$	3 (9)	(36.8)	134.5	
45	$C^0=C^0$	(a) derived from Fig. 1	23.5	147.5	
		(b) derived from the estimate based on the Dewar and Schmeising scheme [10]	(18)	153	
46	$C^1\equiv C^1$	3 (1); basic term taken from Dewar and Schmeising [10]	85.70	171.2	1.204 ± 0.002
47	$C^1_2\equiv C^1_2$	3 (14,16,34)	86.82 ± 0.32	170.1	
48	$C^1_\phi\equiv C^1_\phi$	3 (25,26,27)	(83.30 ± 0.09)	173.6	

(continued)

Table 1. (continued)

Steric Interactions and Conjugation Energy Terms

(1)	(2)	(3)	(4)	(5)	(6)
	1-3 interaction corrections				
1	$[C_3^3 \, C \, C_3^3]$	Part I	0.00 ± 0.2		
2	$[C_3^3 \, C \, C^2]$	2 (37-Δ)	0.00 ± 0.2		
3	$[C_4^3 \, C \, C^2]$	2 (38-Δ)	0.00 ± 0.2		
4	$[C_4^3 \, C \, C_3^2]$	2 (48-Δ)	0.68		
5	$[C_4^3 \, C \, C_3^3]$	Part I (3 alkanes)	1.74 ± 0.2		
6	$[C_4^3 \, C \, C_4^3]$	Part I (2 alkanes)	5.26 ± 0.1		
	cis-interaction corrections				
1	cis $[C_1^3 \, C_1^3]$	2 (4-5,8-9,22-Δ,23-Δ,24-25,	0.93 ± 0.2		
	cis $[C_1^3 \, C^2]$	30-Δ,31-32,33-34)	0.93 ± 0.2		
	cis $[C_1^3 \, C^3]$		0.93 ± 0.2		
	cis $[C_2^3 \, C_2^2]$		0.93 ± 0.2		
2	cis $[C^1 \, C^2]$	3 (18-19,21-22)	-0.15 (cis more stable)		
3	cis $[C^2 \, C^3]$	Ref. 26	1.0		
4	cis $[C^\phi \, C^3]$	4 (32-33)	1.0		
5	cis $[C_4^3 \, C_1^3]$	2 (40-41,41-Δ,49-Δ)	3.84 ± 0.1		
6	cis $[C_4^3 \, C^2]$	2 (45-46,46-Δ)	4.50		

| 7 | cis [C_4^3 C_4^3] | 2 (51-52,52-Δ) | 10.78 |
| 8 | cis [C^ϕ C^ϕ] | 4 (38-39,79-80) | ≈6 |

ortho- and trans-sextet interaction corrections

1	ortho [C_1^3 C_1^3]	4 (4-6,12-13,14,19-20-21)	0.53 ± 0.14
2	ortho [C_1^3 C_2^3]	4 (9-10-11)	0.90 ± 0.15
3	ortho [C_1^3 C_4^3]	4 (22-23-24)	5.3 ± 0.3
4	ortho [C_4^3 C_4^3]	4 (28-29)	≈18
5	trans-sextet [1-5(H...H)]	4 (47-50)	7 ± 0.5
6	trans-sextet [1-5(C_1^3 C_1^3)]	4 (68-69)	18 ± 1
7	trans-sextet [1-4(C_1^3 C_1^3)]	4 (Δ-67, Δ-71, Δ-100)	13 ± 0.5
8	trans-sextet reinforcement (ref. 100)	4(100-101)	≈ 3.6
9	[nonbenzenoid aromatic sextet]	4 (44,46,49)	2.0
10	[beta-substitution in polynuclear aromatic, unsubstituted hydrocarbons]	4 (65)	-0.2

Table 1. (continued)

(1)	(2)	(3)	(4)	(5)	(6)
		Long-range aromatic conjugation energy			
1		$[(C_2^2)_{\phi'} = (C_2^2 - C_2^2)_n = (C_2^2)_{\phi'}]_{n=0,1,2,\dots}$ $4(39,80,85,88)$	-4.0		
2		$[(C_2^1)_{\phi} = (C_2^2 - C_2^2)_n = (C_2^1)_{\phi}]_{n=0,1,2,\dots}$ $3(28)$	-2.0		

Ring Strain Corrections (to appear in Part III)

a Bold face numbers in this column indicate the table number followed by compound numbers in parentheses.

b The absolute bond energies have been calculated on the basis of the most recent NBS values of enthalpies of atomization of carbon and hydrogen as 171.29 and 52.10 kcal/mole, respectively [86].

c Bond distances taken from the standard compilation of the Chemical Society (London) [87].

enthalpy of phase change. Where such values were not available, empirical
group-contribution procedures have been employed. For estimation of the
heat of vaporization the procedure of Small [16] has been used generally,
in the absence of either vapor pressure data or a value of the enthalpy cor-
related through other standard established procedures used in the API-Project
44 compilation [21] or Driesbach's monographs [18]. In Small's method,
the quantity $(EV)^{\frac{1}{2}}$ has been shown to follow an additive correlationship
(the Scatchard equation) with structure, where E is the cohesive energy, i.e.,
the internal energy of vaporization $(\Delta H_V^0 - RT)$, and V the molar volume
derived either from the observed density at 25°C or from a correlation pro-
cedure of Bondi [17] on van der Waals volume. Molar attraction constants
(F) at 25°C have been provided for various structural groups, whereby
$\Delta H_V(25°C) = (\Sigma F)^2/V + R(298)$ is calculated. The method is particularly
valuable for estimating the heat of vaporization of a polymer repeat unit,
a hypothetical but important quantity. Several new group-contribution
terms (F's) have now been added to this scheme on the basis of recent
heat of vaporization data; these will be reported in a separate publication.

For calculating the heat of sublimation, the procedure of Bondi [17],
which gives an estimate of this quantity at the lowest first-order transition
temperature, has been used. Since the heat of sublimation is insensitive
to temperature due to the compensating temperature effects on the two
component enthalpies (fusion and vaporization, as discussed by Cottrell,
Ref. 70, p. 145), the estimate of the heat of sublimation at the lowest
transition is straightway assumed for the temperature (298°K) of this
work. The heat of sublimation so calculated from group contribution,
although self-consistent, was found to be associated, however, with a high
uncertainty of at least ±1 kcal/mole (sometimes up to 3 kcal/mole,
particularly for condensed polynuclear aromatic hydrocarbons where the
data was needed most. Therefore, the over-all uncertainty in $\Delta H_f^0(g)$
observed, for aromatic hydrocarbons in Table 4, is roughly assessed as
±1.5 kcal/mole in sharp contrast to the data on alkanes (Part I) and
alkenes with only ±0.5 kcal/mole. Values parenthesized have higher un-
certainty, exceeding ±2 kcal/mole. The original combustion data and
the uncertainties assigned by the experimental workers are also compiled
in Tables 2 to 5 to enable readers to check any incorrect gas-phase value
arising from an incorrect estimate of the heat of phase change. The
general procedure adopted in deriving the bond-energy terms from the
gas-phase data is as follows:

(a) The compounds are grouped by a common structural feature (e.g., a

Table 2. Alkenes: Heats of Formation (kcal/mole; 298.15°K; 1 atm)

				$\Delta H_f^{\circ}(g)$, estimated				
				Skinner [22]	Franklin [20]	This work	This work	
No.	Hydrocarbon	$\Delta H_f^{\circ}(x)$, experimental[a]	$\Delta H_f^{\circ}(g)$ observed[b]	$(\Delta\Delta)$[d]	$(\Delta\Delta)$[d]	$(\Delta\Delta)$[d]	(Δ)[e]	References
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	Ethylene	12.50 ± 0.07(g)	12.50		0.00	0.02	12.48	10,21,22
2	Propylene	4.88 ± 0.12(g)	4.88	0.00	0.00	-0.02	4.90	40,21,22
3	1-Butene	-0.15 ± 0.2(g)	-0.15	0.10	-0.10	0.04	-0.19	88,21,22
4	2-Butene, *cis*	-1.67 ± 0.2(g)	-1.67	0.07	-0.29	0.08	-1.75	(41),h22,88
5	2-Butene, *trans*	-2.67 ± 0.2(g)	-2.67	0.07	-0.26	0.01	-2.68	(41),h22,88
6	2-Methylpropene	-4.04 ± 0.2(g)	-4.04	0.00	-0.69	-0.08	-3.96	(41),h22,88
7	1-Pentene	-5.00 ± 0.43(g)	-5.00	-0.02	-0.03	0.10	-5.10	(41),h21,22
8	2-Pentene, *cis*	-6.71 ± 0.25(g)	-6.71	-0.04	-0.42	0.13	-6.84	(41),h26,22
9	2-Pentene, *trans*	-7.59 ± 0,25(g)	-7.59	0.08	-0.25	0.18	-7.77	(41),h26,22
10	2-Methyl-1-butene	-8.68 ± 0.25(g)	-8.68	0.06	-0.40	0.17	-8.85	(41),h22
11	3-Methyl-1-butene	-6.92 ± 0.25(g)	-6.92	0.09	-0.59	0.20	-7.12	(41),h22
12	2-Methyl-2-butene	-10.17 ± 0.25(g)	-10.17	0.09	0.00	0.35	-10.52	(41),h22
13	1-Hexene	-17.28 ± 0.24(l)	-9.96	-0.05	-0.06	0.05	-10.01	(34),h43,(25)
14	2-Hexene, *cis*	-20.04 ± 0.24(l)	(-12.51)*	-0.91	-1.30	-0.76	-11.75	23,(25)
15	2-Hexene, *trans*	-20.43 ± 0.31(l)	-12.88	-0.28	-0.61	-0.02	-12.68	23,(25)
16	3-Hexene, *cis*	-18.85 ± 0.23(l)	-11.38	0.22	-0.17	0.55	-11.93	23,(25)
17	3-Hexene, *trans*	-20.55 ± 0.23(l)	-13.01	-0.41	-0.75	-0.15	-12.86	23,(25)

18	2-Methyl-1-pentene	-21.48 ± 0.22(l)	-14.19	-0.52	-0.99	-0.43	-13.76	23,(25)
19	3-Methyl-1-pentene	-18.66 ± 0.29(l)	-11.82	0.12	-0.56	-0.11	-11.71	23,(25)
20	4-Methyl-1-pentene	-19.19 ± 0.37(l)	(-12.24)*	-0.30	-0.98	-0.73	-11.51	23,(25)
21	2-Methyl-2-pentene	-23.54 ± 0.27(l)	(-15.98)*	-0.79	-0.88	-1.30	-14.68	23,(25)
22	3-Methyl-2-pentene, cis	-22.55 ± 0.28(l)	-14.86	-0.25	0.24	-0.36	-14.50	23,(25)
23	3-Methyl-2-pentene, trans	-22.59 ± 0.21(l)	-15.08	-0.47	0.02	0.35	-15.43	23,(25)
24	4-Methyl-2-pentene, cis	-20.78 ± 0.18(l)	-13.73	-0.10	-1.16	0.04	-13.77	23,(25)
25	4-Methyl-2-pentene, trans	-21.86 ± 0.24(l)	-14.69	-0.06	-1.07	0.01	-14.70	23,(25)
26	2-Ethyl-1-butene	-20.80 ± 0.28(l)	-13.38	0.06	-0.18	0.38	-13.76	23,(25)
27	2,3-Dimethyl-1-butene	-22.84 ± 0.34(l)	-15.85	-1.02	-1.29	-0.32	-15.53	23,(25)
28	3,3-Dimethyl-1-butene	-21.08 ± 0.30(l)	-14.25	0.26	0.31	-0.54	-13.71	23,(25)
29	2,3-Dimethyl-2-butene	-24.47 ± 0.27(l)	-16.68	-0.50	-0.77	0.00	-16.68	23,(25)
30	1-Heptene	-23.41 ± 0.20(l)	-14.89	-0.05	-0.07	0.03	-14.92	43,22
31	2-Heptene, cis	-16.90 ± 0.10(g)	-16.90		-0.76	-0.24	-16.66	(26)i
32	2-Heptene, trans	-17.60 ± 0.10(g)	-17.60		-0.40	-0.01	-17.59	(26)i
33	3-Heptene, cis	-16.74 ± 0.10(g)	-16.74		0.56	0.10	-16.84	(26)i
34	3-Heptene, trans	-17.60 ± 0.10(g)	-17.60		0.41	0.17	-17.77	(26)i

(continued)

Table 2. (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
35	3-Methyl-3-hexene, cis	−27.90 ± 0.22(l)	−19.22	0.32	0.80	0.37	−19.59	24,(27),22
36	3-Methyl-3-hexene, trans	−27.13 ± 0.21(l)	(−18.60)*	0.94	1.42	0.99	−19.59	24,(27),22
37	2,4-Dimethyl-1-pentene	−28.15 ± 0.40(l)	−20.27	0.36	−0.78	−0.10	−20.17	24,(27),22
38	4,4-Dimethyl-1-pentene	−26.61 ± 0.40(l)	−19.20	0.91	0.29	−0.05	−19.15	24,(27),22
39	2,4-Dimethyl-2-pentene	−29.60 ± 0.60(l)	−21.44	0.71	−0.06	0.17	−21.61	24,(27),22
40	4,4-Dimethyl-2-pentene, cis	−25.35 ± 0.29(l)	−17.60	−0.33	3.20	−0.15	−17.45	24,(27),22
41	4,4-Dimethyl-2-pentene, trans	−29.28 ± 0.20(l)	−21.46	−0.03	0.39	−0.17	−21.29	24,(27),22
42	2-Ethyl-3-methyl-1-butene	−27.44 ± 0.32(l)	(−19.25)*	−0.95	0.24	1.19	−20.44	24,(27),22
43	2,3,3-Trimethyl-1-butene	−28.31 ± 0.28(l)	−20.67	−0.00	2.12	0.00	−20.67	24,(27),22
44	1-Octene	−29.52 ± 0.20(l)	−19.82	−0.05	−0.07	0.01	−19.83	43,22

45	2,2-Dimethyl-3-hexene, cis	-30.59 ± 0.57(l)	-21.77	0.43	3.96	0.11	-21.88	24,(27),22
46	2,2-Dimethyl-3-hexene, trans	-35.01 ± 0.29(l)	-26.16	0.20	0.62	0.22	-26.38	24,(27),22
47	3-Ethyl-2-methyl-1-heptene	-33.29 ± 0.18(l)	-24.40	0.29	0.21	0.31	-24.71	24,(27),22
48	2,4-Trimethyl-1-pentene	-35.18 ± 0.16(l)	-26.68		1.04	0.00	-26.68	24,(27),22
49	2,4,4-Trimethyl-2-pentene	-34.41 ± 0.43(l)	-25.50	-0.01	4.11	-0.21	-25.29	24,(27),22
50	1-Decene	-29.48 ± 0.2(l)	-29.67	0.18	-0.07	-0.02	-29.65	43,22
51	2,2,5,5-Tetramethyl-3-hexene, cis	-39.09 ± 0.41(l)	-28.92	-0.02	(11.32)	0.20	-29.12	24,22
52	2,2,5,5-Tetramethyl-3-hexene, trans	-49.62 ± 0.59(l)	-39.43	0.69	1.86	0.47	-39.90	24,22
53	2,4,4,6,6-Penta-methyl-2-heptene		-46.0†			0.72	-46.72	29
54	2,4,4,6,8,8-Hepta-methyl-2-nonene		-63.7†			0.16	-63.86	29
55	1-Hexadecene	-78.73 ± 0.44(l)	-59.55		-0.39	-0.44	-59.11	42,(21)
56	5-Methyl-1-hexene	-24.34 ± 0.2(l)	-16.15			0.07	-16.24	38,(18)
	Standard deviation[u]	±0.30	±0.5	±0.33	±1.20	±0.25		
	Confidence limits[u]	±0.60		±0.7	±2.5	±0.5		

(continued)

Footnotes to Table 2.

a Original experimental data in phase (x); where (c) = condensed solid, (c') = partly crystalline solid, (c'') = fully crystalline solid, (l) = liquid, (gl) = glassy state (supercooled liquid), (g) = ideal gas. Where the experimental value pertains to reaction other than combustion, a parenthesized reference with superscript letter indicating the type of reaction will be found in the last column.

b The best value derived for the ideal gas phase, combining the experimental value of the heat of formation in phase (x) and the enthalpy of phase change; the latter quantity is an observed one where a reference is given in parenthesis (without superscript letter). In all other cases, the enthalpy of phase change is an estimate by this author using group-contribution or other method shown by an underlined reference in parenthesis.

d Expressed as the difference: $\Delta\Delta H_f^\circ (obsd - estd)$.

e Expressed as the actual value: $\Delta H_f^\circ(g)$.

h Hydrogenation calorimetry.
i Isomerization equilibrium.
u Uncertainty assignment as discussed by Rossini [44].
* Parenthesized data are possibly associated with experimental uncertainty > 1 kcal/mole.
† Underlined data represent values derived from other empirical schemes.

Table 3. Alkadienes and Alkynes: Heats of Formation (kcal/mole; 298.15°K; 1 atm)

No.	Hydrocarbon	$\Delta H^\circ_f(x)$ experimental[a]	$\Delta H^\circ_f(g)$ observed[b]	$\Delta H^\circ_f(g)$ estimated Franklin (20) $(\Delta\Delta)$[d]	This work $(\Delta\Delta)$[d]	This work (Δ)[e]	References
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	Propadiene (allene)	45.92 ± 0.75(g)	45.9	0.00	-0.5	46.39	(30),h31
2	1,2-Butadiene	38.77 ± 0.75(g)	38.8	–	0.0	38.81	88,31
3	1,3-Butadiene	26.00 ± 0.19(g)	26.0	-3.95	-0.2	26.15	88,30
4	1,2-Pentadiene	33.61 ± 0.16(g)	33.6	–	-0.1	33.72	45
5	1,3-Pentadiene, cis	19.77 ± 0.22(g)	19.8	-3.99	0.2	19.57	45
6	1,3-Pentadiene, trans	18.77 ± 0.16(g)	18.8	-3.94	0.2	18.57	(32),i45,31
7	1,4-Pentadiene	25.41 ± 0.31(g)	25.4	-0.66	0.4	24.96	45
8	2,3-Pentadiene	31.79 ± 0.17(g)	31.8	–	0.6	31.23	45
9	3-Methyl-1,2-butadiene	24.18 ± 0.12(l)	30.8	–	0.0	30.81	46
10	2-Methyl-1,3-butadiene (isoprene)	11.00 ± 0.38(l)	17.3	-4.47	0.1	17.24	81,(18)
11	Acetylene (ethyne)	54.19 ± 0.19(g)	54.2	0.01	0.0	54.20	33
12	Propyne	44.32 ± 0.20(g)	44.3	0.00	-0.1	44.42	33
13	1-Butyne	39.48 ± 0.21(g)	39.5	0.11	0.00	39.51	88
14	2-Butyne	35.37 ± 0.35(g)	35.4	0.93	-0.4	35.76	33,88

15	1-Pentyne	34.50 ± 0.50(g)	34.5	0.03	-0.1	34.60	33
16	2-Pentyne	30.80 ± 0.50(g)	30.8	1.24	0.0	30.85	33
17	3-Methyl-1-butyne	32.60 ± 0.50(g)	32.6	-0.51	0.0	32.60	33
18	3-Penten 1-yne, cis	54.24 ± 0.50(l)	60.2	-2.96	0.0	60.18	(34),h(16)
19	3-Penten-1-yne, trans	54.64 ± 0.50(l)	60.4	-1.81	0.1	60.33	(34),h(16)
20	1,5-Hexadiyne (dipropargyl)	91.88 ± 1.00(l)	99.4	0.41	0.0	99.45	(34),h(16)
21	3-Decen-1-yne, cis	23.67 ± 0.3(l)	35.4	-0.20	0.0	35.45	(34),h(16)
22	3-Decen-1-yne, trans	23.97 ± 0.3(l)	35.5	-2.05	-0.1	35.60	(34),h(16)
23	5,7-Dodecadiyne	43.09 ± 0.7(l)	55.8	-3.73	0.0	55.85	(36),h(16)
24	Ethynylbenzene	67.72 ± 1.00(l)	77.7	1.21	0.0	77.72	(35),h(16)
25	Diphenyldiacetylene	74.50 ± 1.0(c)	98.8	0.03	0.0	98.84	37,(17)
26	Di(o'-tolyl)acetylene	55.93 ± 2.0(c)	84.0	-0.29	-0.1	84.14	37,(17)
27	Di(p'-tolyl)acetylene	53.78 ± 2.0(c)	83.2	0.06	0.1	83.08	37,(17)
28	Diphenylbutadiene	123.73 ± 1.0(c)	151.9	-1.57	0.0	151.91	37,(17)
29	Butadiyne (biacetylene)		(113.0)*	(4.12)	(10)	103.13	(19)r
30	1-Buten-3-yne (vinyl acetylene)		(72.8)	0.53	(5)	67.91	39,19
31	1,5-Hexadiene	12.54 ± 0.1(l)	20.0	-1.15	0.0	20.05	38,19
32	1,7-Octadiyne	80.0 ± 1.2(l)	89.6	0.42	0.0	89.63	(36),h(16)
33	3,9-Dodecadiyne	46.98 ± 0.5(l)	61.4	1.84	-0.7	62.05	(36),h(16)
34	2,4-Hexadiyne	79.0 ± ? (l)	86.2	-2.92	0.4	85.75	19,(16)

(continued)

Table 3. (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
35	1-Octen-3-yne	33.66 ± 1.50(l)	43.7	-1.08	-0.6	44.30	(35),h(18)
36	Butatriene		(64.4)*	(-4.94)	(-5)	69.5†	51
	Standard deviation[u]	±0.80	±1.0	±2.0	±0.25		
	Confidence limits[u]	±1.60		±4.0	±0.50		

a Original experimental data in phase (x); where (c) = condensed solid, (c') = partly crystalline solid, (c'') = fully crystalline solid, (l) = liquid, (gl) = glassy state (supercooled liquid), (g) = ideal gas. Where the experimental value pertains to reaction other than combustion, a parenthesized reference with superscript letter indicating the type of reaction will be found in the last column.

b The best value derived for the ideal gas phase, combining the experimental value of the heat of formation in phase (x) and the enthalpy of phase change; the latter quantity is an observed one where a reference is given in parenthesis (without superscript letter). In all other cases, the enthalpy of phase change is an estimate by this author using group-contribution or other method shown by an underlined reference in parenthesis.

d Expressed as the difference: $\Delta\Delta H_f^\circ (obsd - estd)$.

e Expressed as the actual value: $\Delta H_f^\circ(g)$.

h Hydrogenation calorimetry.

i Isomerization equilibrium.

r Reaction calorimetry.

u Uncertainty assignment as discussed by Rossini [44].

* Parenthesized data are associated with high experimental uncertainty of ±2 kcal/mole or higher.

† Underlined data represent value derived from other empirical schemes.

Table 4. Aromatic, Partially Aromatic, and Polynuclear Hydrocarbons: Heats of Formation (kcal/mole; 298.15°K; 1 atm)

No.	Hydrocarbon	$\Delta H_f^\circ(x)$ experimental[a]	$\Delta H_f^\circ(g)$ observed[b]	$\Delta H_f^\circ(g)$ estimated			References
				Franklin (20) ($\Delta\Delta$)[d]	This work ($\Delta\Delta$)[d]	This work (Δ)[e]	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	Benzene	11.72 ± 0.12(l)	19.82	0.02	0.0	19.80	47,48,21
2	Toluene	2.87 ± 0.15(l)	11.95	0.00	0.0	11.92	47,48,21
3	Ethylbenzene	-2.98 ± 0.20(l)	7.12	0.10	0.1	7.01	48,21
4	1,2-Dimethylbenzene	-5.84 ± 0.26(l)	4.54	-0.16	0.0	4.57	48,21
5	1,3-Dimethylbenzene	-6.08 ± 0.18(l)	4.12	0.02	0.1	4.04	48,21
6	1,4-Dimethylbenzene	-5.84 ± 0.24(l)	4.29	0.19	0.3	4.04	48,21
7	n-Propylbenzene	-9.18 ± 0.20(l)	1.87	-0.23	-0.2	2.10	48,21
8	i-Propylbenzene (cumene)	-9.85 ± 0.26(l)	0.94	0.20	0.3	0.60	49,21
9	2-Ethyl-1-methylbenzene	-11.11 ± 0.26(l)	0.29	-0.28	-0.1	0.34	49,21
10	3-Ethyl-1-methylbenzene	-11.67 ± 0.28(l)	-0.46	0.37	0.4	-0.87	49,21
11	4-Ethyl-1-methylbenzene	-11.92 ± 0.34(l)	-0.79	0.05	0.1	-0.87	49,21
12	1,2,3-Trimethylbenzene	-14.01 ± 0.30(l)	-2.29	0.06	0.5	-2.78	49,21
13	1,2,4-Trimethylbenzene	-14.79 ± 0.27(l)	-3.33	-0.18	0.0	-3.31	49,21
14	1,3,5-Trimethylbenzene	-15.18 ± 0.34(l)	-3.84	-0.09	0.0	-3.84	49,21
15	n-Butylbenzene	-15.28 ± 0.30(l)	-3.30	-0.47	-0.5	-2.81	50
16	i-Butylbenzene	-16.70 ± 0.32(l)	(-5.15)	-0.96	-0.8	-4.31	50
17	s-Butylbenzene	-15.89 ± 0.30(l)	-4.17	0.02	-0.2	-3.99	50

18	t-Butylbenzene	-16.92 ± 0.30(l)	-5.42	2.07	0.0	-5.42	50
19	1,2,3,4-Tetramethylbenzene	-23.04 ± 0.71(l)	-10.0†	-0.42	0.1	-10.13	50
20	1,2,3,5-Tetramethylbenzene	-23.54 ± 0.71(l)	-10.7†	-0.51	0.0	-10.66	50
21	1,2,4,5-Tetramethylbenzene	-23.58 ± 0.78(l)	-10.8†	-0.42	-0.1	-10.66	50
22	2-(t-Butyl)-1-methylbenzene		-8.00	(5.94)	0.0	-8.0	52
23	3-(t-Butyl)-1-methylbenzene		-13.0	1.15	0.3	-13.30	52
24	4-(t-Butyl)-1-methylbenzene		-13.6	1.75	-0.3	-13.30	52
25	Pentamethylbenzene	-32.44 ± 0.3(c)	-17.8	-0.94	-0.3	-17.48	53
26	Hexamethylbenzene	-39.19 ± 0.60(c)	(-25.3)	-0.76	-1.0	-24.30	53
27	Bibenzyl	12.31 ± 0.31(c)	34.5	-4.41	0.0	34.45	58,(73)
28	1,2,4-Tri(t-butyl)benzene	-60.14 ± 0.8(c)	-37.3	(22.77)	0.6	-37.9	54
29	1,3,5-Tri(t-butyl)benzene	-76.94 ± 0.9(c)	-55.1	(5.57)	0.8	-55.86	54
30	Styrene (ethynylbenzene)	24.91 ± 0.14(l)	35.3	-1.75	-0.1	35.40	55
31	α-Methylstyrene (2-propenyl-benzene)	16.84 ± 0.13(l)	27.8	0.00	1.3	26.50	56
32	1-Propenylbenzene, cis	29.00 ± 0.75(g)	29.00†	-1.83	0.2	28.82	30
33	1-Propenylbenzene, trans	28.00 ± 0.75(g)	28.0	-1.88	0.2	27.82	30
34	1-Methyl-2-ethenylbenzene	28.30 ± 0.75(g)	28.3	-1.52	-0.1	28.42	30
35	1-Methyl-3-ethenylbenzene	27.60 ± 0.75(g)	27.6	-1.62	0.1	27.52	30
36	1-Methyl-4-ethenylbenzene	27.40 ± 0.75(g)	27.4	-1.82	-0.1	27.52	30
37	1,1-Diphenylethylene	40.50 ± 0.14(l)	57.0	-4.03	0.1	56.94	57,(16)
38	1,2-Diphenylethylene, cis (isostilbene)	43.16 ± 0.18(l)	59.9	-3.10	-0.4	60.34	57,(16)
39	1,2-Diphenylethylene, trans (stilbene)	32.88 ± 0.12(c)	54.2	(-7.87)	-0.1	54.34	57,(17)

(continued)

Table 4. (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
40	Triphenylethylene	54.96 ± 0.19(c)	84.9	-1.50	-1.0	85.87	57,(17)
41	Tetraphenylethylene	73.40 ± 0.14(c)	112.0	-0.85	-1.4	113.40	57,(17)
42	Biphenyl	24.02 ± 0.36(c)	42.4	-1.79	0.0	42.45	58,(72)
43	Naphthalene	18.57 ± 0.25(c)	36.0	1.03	0.1	35.85	58
44	Anthracene	30.87 ± 0.44(c)	54.3	-4.18	0.4	53.90	58,(74)
45	Phenanthrene	27.76 ± 0.34(c)	49.5	-0.66	0.0	49.47	58
46	Naphthacene	38.05 ± 0.32(c)	69.8	2.45	-0.2	69.95	59,(76)
47	Chrysene	34.82 ± 0.49(c)	62.9	-2.38	-0.2	63.09	59
48	Triphenylene	33.70 ± 0.11(c)	61.1	(-4.18)	0.4	60.66	60
49	1,2-Benzanthracene	40.93 ± 0.56(c)	67.0	1.73	-0.5	67.52	59
50	3,4-Benzophenanthrene	44.29 ± 0.45(c)	69.7	4.39	-0.4	70.09	59
51	Pyrene	27.41 ± 0.09(c)	50.7	(-7.97)	-1.0	51.67	60
52	Perylene	43.66 ± 0.11(c)	77.2	-1.84	-0.2	77.40	60
53	Fluoranthene	45.36 ± 0.09(c)	69.2	-0.26	0.2	68.95§	60,62
54	Biphenylene	84.4 ± 0.7(c)	(105)	(50)	-0.3	(105.3)§	61,(17)
55	Acenaphthylene	44.7 ± 1.1(c)	61.7	-2.36	0.5	62.17§	62
56	Indene	26.39 ± 0.30(l)	38.6	0.33	-2.3	40.89§	63,(75),h(77)
57	Acenaphthene	16.8 ± 0.6(c)	37.4	2.07	1.9	35.50§	62
58	Indan (hydrindane)	2.56 ± 0.47(l)	14.6	-0.64	0.0	14.54§	63,(77)
59	Fluorene	20.8 ± 2.0(c)	(43.76)*	0.00	–	(47.81)§	66,13,(72)
60	5,12-Dihydronaphthacene	25.54 ± 0.33(c)	54.4	(4.4)	-0.4	54.77	59
61	9,10-Dihydroanthracene	15.98 ± 0.28(c)	37.4	-1.42	-0.7	38.06	59
62	9,9'-Bianthryl	78.13 ± 0.75(c)	(113.5)*	(8.72)	(3.4)	110.05	59

63	9,9′-Biphenanthryl	51.02 ± 0.66(c)	(87.2)*	(-17.58)	—	101.79	59
64	α-Methylnaphthalene	13.34 ± 0.40(l)	28.0	0.82	0.0	27.97	64
65	β-Methylnaphthalene	10.72 ± 0.35(l)	27.8	0.64	0.0	27.77	64
66	2,7-Dimethylphenanthrene	8.69 ± 0.56(c)	34.2	0.22	0.5	33.71	65,100
67	4,5-Dimethylphenanthrene	21.25 ± 1.40(c)	46.3	(10.98)	-0.4	46.71	65,100
68	5,8-Dimethylbenzo-phenanthrene	25.86 ± 1.28(c)	55.3	(5.72)	1.0	54.34	65,(17)
69	1,12-Dimethylbenzo-phenanthrene	36.91 ± 0.92(c)	(66.3)	(16.72)	1.0	(65.3)	65,(17)
70	3,9-Dimethylbenzanthracene	18.20 ± 0.67(c)	48.3	-1.28	-1.5	49.76	65,(17)
71	1,12-Dimethylbenzanthracene	33.20 ± 0.67(c)	(63.3)	(13.92)	-1.8	(65.1)	65,(17)
72	9,10-Diphenylanthracene	73.91 ± 0.69(c)	(105.9)*	(7.1)	—	99.50	59,(17)
73	1,4-Dihydronaphthalene	18.8 ± 1.0(c)	33.3	-0.60	1.2	32.04	19,(17)
74	1,2-Dihydronaphthalene	16.5 ± 1.0(c)	30.3	-0.60	-0.1	30.37	19,(17)
75	Tetralene		(2.6)*	-2.04	-2.2	4.83	66
76	Benzocyclobutene	44.6 ± 0.5(g)	44.6	1.4	0.0	44.65	(67)h
77	Diphenylmethane	23.05 ± 0.2(c) 21.25 ± 0.32(l)	39.0	-0.2	0.4	39.36	38,71,(16,17)
78	1,1-Di(p-tolyl)ethylene	20.36 ± 0.48(c)	44.1	(-4.2)	-0.1	41.18	68,(17)
79	1,2-Di(p-tolyl)ethylene, cis	23.22 ± 0.48(c)	45.6	-1.7	0.0	44.58	68,(17)
80	1,2-Di(p-tolyl)ethylene, trans	13.66 ± 0.48(c)	38.0	(-8.3)	-0.6	38.58	68,(17)
81	Tri(p-tolyl)ethylene	28.71 ± 0.72(c)	61.8	-1.1	-0.4	62.23	68,(17)
82	Tetra(p-tolyl)ethylene	40.64 ± 0.96(c)	83.4	1.9	1.5	81.88	68,(17)
83	1,1-Di(o-tolyl)ethylene	21.07 ± 0.48(c)	43.5	-3.0	1.3	42.24	68,(17)
84	1,2-Di(o-tolyl)ethylene, cis	20.36 ± 0.48(c)	(42.5)*	(-6.0)	-3.1	45.64	68,(17)
85	1,2-Di(o-tolyl)ethylene, trans	17.73 ± 0.48(c)	40.8	(-6.8)	1.2	39.64	68,(17)

(continued)

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Table 4. (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
86	Tri(o-tolyl)ethylene	29.66 ± 0.72(c)	(60.8)*	-3.9	-3.0	63.82	68,(17)
87	1,4-Diphenylbutadiene, cis,cis	47.33 ± 0.48(c)	71.4	(-9.5)	-0.6	72.00	68,(17)
88	1,4-Diphenylbutadiene, trans,trans	42.55 ± 0.24(c)	68.6	(-11.4)	0.6	68.00	68,(17)
89	1,1,4,4-Tetraphenyl-1,3-butadiene	78.53 ± 0.72(c)	(119.4)*	(-9.3)	—	(115.07)	68,(17)
90	1,2,3,4-Tetraphenylbutadiene, trans,trans	85.46 ± 0.72(c)	(128.3)*	(4.4)	—	(115.07)	68,(17)
91	1,1-Diphenylethane	11.48 ± 0.48(c)	32.5	0.4	-0.5	32.95	69,(17)
92	1,2-Diphenylethane	11.72 ± 0.24(c)	32.5	-1.8	-2.0	34.45	69,(17)
93	1,1,1-Triphenylethane	37.37 ± 0.48(c)	58.5	1.6	1.4	57.09	69,(17)
94	1,1,2-Triphenylethane	30.92 ± 0.48(c)	59.9	-0.3	-0.5	60.39	69,(17)
95	1,1,1,2-Tetraphenylethane	54.17 ± 0.72(c)	(91.3)*	(6.1)	—	84.53	69,(17)
96	1,1,2,2-Tetraphenylethane	52.49 ± 0.72(c)	89.6	3.5	3.3	86.33	69,(17)
97	Pentaphenylethane	90.80 ± 0.72(c)	(136.0)*	(25.9)	—	110.47	69,(17)
98	Triphenylmethane	38.71 ± 1.4(c)	65.7	0.6	0.4	65.30	38,53,(17)
99	Tetraphenylethane	57.88 ± 0.6(c)	90.0	0.9	0.6	89.44	38,(17)
100	2,4,5,7-Tetramethyl-phenanthrene	3.8 ± 0.8(c)	31.1	(12.4)	0.2	30.95	100
101	3,4,5,6-Tetramethyl-phenanthrene	6.4 ± 0.7(c)	38.3	(19.6)	0.2	38.15	100

102	Picene		80.44	76.7	Predicted value
103	Aceanthrylene		79.22	79.9	Predicted value
104	Acephenanthrylene		79.22	75.8	Predicted value
105	Coronene		90.90	81.7	Predicted value
106	Ovalene		119.3	97.3	Predicted value
107	Tetraphenylene		97.3	103.8	Predicted value
	Standard deviation[u]	±0.60	+1.5	±0.97	
	Confidence limits[u]	±1.2	+1.77 +3.5	±2.0	

a Original experimental data in phase (x); where (c) = condensed solid, (c') = partly crystalline solid, (c'') = fully crystalline solid, (1) = liquid, (gl) = glassy state (supercooled liquid), (g) = ideal gas. Where the experimental value pertains to reaction other than combustion, a parenthesized reference with superscript letter indicating the type of reaction will be found in the last column.

b The vest value derived for the ideal gas phase, combining the experimental value of the heat of formation in phase (x) and the enthalpy of phase change; the latter quantity is an observed one where a reference is given in parenthesis (without superscript letter). In all other cases, the enthalpy of phase change is an estimate by this author using group-contribution or other method shown by an underlined reference in parenthesis.

d Expressed as the difference: $\Delta\Delta H_f^\circ$ (obsd – estd).

e Expressed as the actual value: ΔH_f°(g).

h Hydrogenation calorimetry.
u Uncertainty assignment as discussed by Rossini [44].
* Parenthesized data are associated with high experimental uncertainty of ±2 kcal/mole or higher.
† Underlined data represent value derived from other empirical schemes.
§ Corrected for (nonaromatic) ring-strain energies taken from Part III (to be published), and trans-sextet interactions given in Table 1.

Table 5. Hydrocarbon Polymers: Heats of Formation (kcal/mole; 298°K; 1 atm)

| | | | | $\Delta H^\circ_f(g)$ estimated | | | |
| | | | | Franklin (20) | This work | | |
No.	Hydrocarbon polymer	$\Delta H^\circ_f(x)$ experimental[a]	$\Delta H^\circ_f(g)$ observed[b]	$(\Delta\Delta)$[d]	$(\Delta\Delta)$[d]	(Δ)[e]	References
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	Poly(1,3-butadiene), cis	3.18 ± 0.79(c)	8.1	-0.93	-0.1	8.17	79,(80)
2	Poly(1,3-butadiene), trans		—	—	—	7.24	79,(80)
3	Poly(isoprene), cistactic, Natural rubber	-6.89 ± 1.44(c)	-1.3	-1.57	-0.4	-0.91	81,(80)
4	Poly(styrene), atactic	8.27 ± 0.20(gl)	16.2	0.22	0.1	16.12	7,82,(80,16)
5	Poly(styrene), isotactic	7.99 ± 0.30(gl)	15.9	—	—	—	7,82,(80,16)
6	Poly(α-methylstyrene)	7.88 ± 0.36(gl)	16.5	(8.7)	0.2	16.70	7,(80,16)
7	Poly(acenaphthylene)	27.13 ± 0.36(gl)	44.0	1.00	-0.3	44.278§	7,(17,16)
8	Poly(carbon), diamond	6.45 ± 0.02(c″)	0.45	—	—	0.90	83
9	Poly(carbon), graphite	0.00 ± 0.01(c″)	2.26	—	0.0	2.33	83,(85,12a)
10	Poly(carbon), "carbene"	-9.53(c″)		(Δ)[e]	—	24.9	84,1
11	Poly(phenylene) ⬡		—	24.34	—	11.90	(89),[P] predicted value
12	Poly(p-xylene) ⬡—C—C—		—	14.49	—	14.65	(89),[P] predicted value

13	Poly(ethenyl-phenylene),				
	cis	—	(43.22)	—	40.54	(89), predicted value
	trans	—	42.17	—	34.54	(89), predicted value
14	Poly(tetramethyl-xylylene)	—	−16.89	—	−15.81	(89), predicted value
15	Poly(diphenylethenyl-phenylene)	—	93.05	—	93.6	(89), predicted value

(continued)

Table 5. (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
	Standard deviation[u]	±0.7		±1.0	±0.25		
	Confidence limits[u]	±1.4		±2.0	±0.5		

[a] Original experimental data in phase (x); where (c) = condensed solid, (c') = partly crystalline solid, (c'') = fully crystalline solid, (l) = liquid, (gl) = glassy state (supercooled liquid), (g) = ideal gas. Where the experimental value pertains to reaction other than combustion, a parenthesized reference with superscript letter indicating the type of reaction will be found in the last column.

[b] The best value derived for the ideal gas phase, combining the experimental value of the heat of formation in phase (x) and the enthalpy of phase change; the latter quantity is an observed one where a reference is given in parenthesis (without superscript letter). In all other cases, the enthalpy of phase change is an estimate by this author using group-contribution or other method shown by an underlined reference in parenthesis.

[d] Expressed as the difference: $\Delta\Delta H_f^\circ(obsd - estd)$.

[e] Expressed as the actual value: $\Delta H_f^\circ(g)$.

[P] Polymerization equilibrium.

[u] Uncertainty assignment as discussed by Rossini [44].

[§] Corrected for (nonaromatic) ring-strain energy taken from Part III (to be published).

typical bond) for which a new bond energy term is being derived; compounds in such groups are listed bondwise in Column 3 of Table 1.

(b) The bond energy contributions of all hydrogen atoms are first eliminated by using the standard bond-energy terms for C—H bonds listed in the first part of Table 1, which have been taken from well-established earlier work [12, 90, 91] and which have a perfect linear relationship between absolute bond energy and bond length.

(c) The balance of the heat of formation is attributed successively to the various new C—C bonds as they occur in groups of compounds. Hydrocarbons with simple bonds are dealt with first, followed by more and more complex types of bonds, and finally by structural group features, such as the strain energy or the conjugation energy terms whch are not ascribable to any particular two-atom bond but prevail over the entire molecule.

(d) The bond-energy term is a simple arithmetic mean of such energies assigned to a particular bond in different compounds in a group, after eliminating the contributions of all other bonds by using energy terms already derived in this work or taken from other well-known theoretical work [10, 11, 90-92] as for the C—H bonds.

(e) The sequence followed in deriving the bond-energy terms from the simple to the complex types of carbon-carbon bonds is purely arbitrary and intuitive, justified only by the ultimate success of the scheme. It is entirely possible to derive another set of self-consistent energy terms from the same observed data by following a different sequence. From a few such initial trials, however, it can be stated that more or less the same values would result from the choice of a different sequence. In future work on calculating the temperature dependence of these energy terms, the same sequence will be observed as followed in this work, and this is very important for self-consistency at all temperatures.

(f) To calculate the absolute energy of the bond from its heat of formation term, the sum of the appropriate fractions of the standard enthalpies of atomization of the two binding elements is taken and the heat of formation of the bond subtracted therefrom. The former quantity is determined by the ratio of the number of valence electrons engaged in the particular bond to the total number of free valence electrons of the atom in the atomized state; for example, for the aromatic bond $C^\phi \overline{\cdots} \ C^\phi$ in benzene, a total number of three electons (1-½ from each carbon) contribute to the hybrid bonding orbital, giving rise to $E^0 = [(\frac{3}{2} + \frac{3}{2})/4 \times (171.29)]$ – X kcal/mole, where X is the heat of formation term, and for $C^\phi_* \overline{\cdots} C^\phi$ and $C^\phi_* \overline{\cdots} C^\phi_*$ bonds in naphthalene the absolute

bond energies are: $E^0 = [(\frac{3}{2} + \frac{4}{3})/4 \times (179.29)] - X$ and $E^0 = [(\frac{4}{3} + \frac{4}{3})/4 \times [179.29)] - X$ kcal/mole, respectively.

Alkenes

In general seven ΔH_f^0 energy terms were necessary for a sp^2-sp^3 single bond to fit in the alkene data within a precision limit of ±0.25 kcal for the calculated values. These terms averaged to about –4.4 ± 0.3 kcal, excluding the hydrocarbons with a quaternary sp^3 carbon where the bond energy was lowered distinctly by about 2 to 3 kcal. The strongest sp^2-sp^3 bond is formed in the case of a tertiary sp^3 carbon atom with –4.9 kcal as the heat of formation. It was also necessary to differentiate between sp^2 carbons, i.e., the one with one hydrogen on it (C_2^2) and the "tertiary" sp^2 carbon (C_3^2), the sp^2-sp^3 bonds with the latter were uniformly weaker (less negative). The bond between the phenyl group and the sp^3 carbon ($C^\phi-C^3$) had about the same energy (–4.24 kcal) as did sp^2-sp^3, except where the sp^3 carbon was quaternary, in which case a bond weaker by about 2kcal was formed.

As regards the 1-3 interactions of a sp^2 carbon with sp^3, denoted by $[C^3 \ C \ C^2]$ in Table 1, the sp^2 carbon with one or two hydrogens (C_2^2 or C_1^2) has the same steric interaction as a C_2^3, namely zero, while a teritary sp^2 (C_3^2) interacts like a C_3^3 -carbon. Thus the repulsive, 1-3 interaction seem to depend on the number of interfering carbon-carbon bonds present on the carbon atom rather than on its hybridization state.

In this paper several cis interaction correction terms (in all about 8) have emerged from new experimental data (26, 24, 22). Except where a quaternary sp^3-carbon or a phenyl group occurs in the cis position, the repulsive cis interaction ranges from 0.5 to 1.0 kcal only. But with two phenyl groups or two tertiary butyl groups (C_4^3-carbon atoms) in the cis position, the interactions are severe, about 6 and over 10 kcal, respectively. Two special cases of "reverse" cis interaction have been noted by Skinner and Snelson [34] from hydrogenation calorimetry, where a cis alkene with an acetylenic carbon (C^1) in the cis position was stabler than a trans alkene by about 0.15 kcal, giving rise to the only negative cis $[C^1 \ C^2]$ term in our Table 1.

The basic energy-term for a carbon-carbon double bond ($C_1^2 = C^2$) was derived from ethylene as 133.3 kcal (in terms of the absolute bond strength), contributing +38.00 kcal to the heat of formation. Two more "special" energy terms for C_2^2- and C_3^2-type double bonds were necessary

to fit in the alkene data more exactly than the over-all general precision of this scheme (±1 kcal) achieved for other compounds.


Alkadienes and Alkynes

Due to the well-known "resonance" or delocalization energy effects in π-electron-hybrid orbitals, carbon-carbon single bonds between two sp^2-carbons (as in alkadienes), or between sp- and sp^2-carbons, or between two sp-carbons (as in alkynes and alkadiynes), are considerably stronger and the corresponding bond lengths shorter. Thus, the C^2-C^2 bond energy term is about -13 kcal; C^1-C^3, -15 to -15.6 kcal; C^1-C^2, -21.6 kcal; followed by the C^1-C^1, -36.8 kcal, which appears to be the strongest carbon-carbon single bond. The conjugation of sp^2 or sp-carbons with a phenyl group follows the same pattern of energy lowering as with the sp^2-carbon. The various bond energy terms related to C^ϕ-carbon bonds are given in Table 1. It is interesting to note that the allene-type of double bond ($C^0=C^2$) is somewhat stronger than a $C^2=C^2$ by about 2 kcal, and the $C^0=C^0$ in buta-triene is considerably stronger by about 15 to 20 kcal. The delocalization effects arising from conjugation of sp or sp^2-carbon with a phenyl group can be long range, extending over four or more conjugated carbons in a chain, as seen from the heat of formation of 1,4-diphenyl butadiene, trans,trans (Table 4, hydrocarbon No. 88, Ref. 68); the magnitudes of these effects are -2 and -4 kcal, respectively, for C^1 and C^2 conjugations, as given in Table 1.

Aromatic Hydrocarbons

For the application of this scheme to polynuclear (fused rings) aromatic hydrocarbons, the following rigorous definitions have been adopted and the bond energy terms derived on the basis of these definitions.

(A) A polycyclic hydrocarbon system is considered "aromatic" (in the general sense of this term), and the special bond-energy terms of aromatic bonds applicable thereto, only if: (1) all rings are six-membered; (2) all the carbon atoms of the ring are either $\cdots \overset{(H)}{C} \cdots$ or $\overset{\diagup}{C} =$; with no $-CH_2-$ bridging anywhere in the molecule, and (3) when a classical Kekulé structure is drawn for the hydrocarbon as described in (B) below, none of the six-membered rings has more than two exo (out-of-ring) double bonds.

(B) Three subcategories of aromatic hydrocarbons are recognized with the help of the classical Kekulé structure with alternate C=C and C–C bonds. These are: ultra-aromatic, aromatic, and subaromatic. The Kekulé structure of the molecule is drawn so as to contain the maximum number of "benzenoid" sextets. A "benzenoid" sextet is the one in which all the six sp²-carbons have endo (in-the-ring) double bonds as in benzene. Of the following three Kekulé diagrams of pyrene, Structure (a) has the maximum number of benzenoid sextets, namely 3, but not structure (b) with 2 nor structure (c) with only 1.
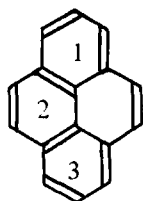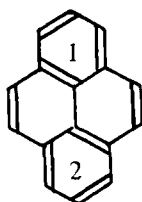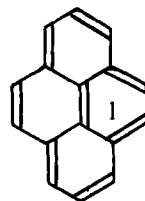
(a)   (b)   (c)

Structures such as (a) only are to be employed for computing the heat of formation by the method given in this work. The subcategories are defined as follows:

(a) Ultra-aromatic. A system is considered ultra-aromatic (meaning perfectly or fully aromatic, extending the ideas of Clar [93]), when in a classical Kekulé structure drawn with the maximum number of benzenoid sextets, no sp²-carbon shall have an exo double bond; for example, phenanthrene (a) in the following diagram:
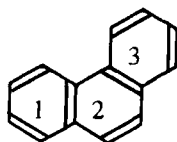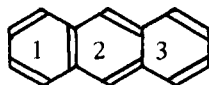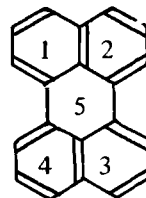
(a)   (b)   (c)

where each of the three sextets viewed independently has a benzenelike structure with all the six carbons having endo double bonds.

(b) Aromatic. A system is considered aromatic (but not ultra-aromatic) when none of the fused rings has more than two sp^2-carbons with exo double bond; for example, anthracene (b) above, where the sextet marked 3 has four endo and two exo double bonded carbons.

(c) Subaromatic. A system is considered subaromatic (or partially aromatic) when any of the fused sextets viewed independently contains more than two exo double bonds; for example, perylene (c) above, the ring marked 5 having all the six carbon atoms with exo double bonds.

With the above definitions, triphenylene, chrysene, and coronene are ultra-aromatic; naphthacene and 1,2-benzanthracene are aromatic; while pyrene, fluoranthene, biphenylene, fluorene, indene, etc. are subaromatic hydrocarbons.

(C) For the aromatic and ultra-aromatic hydrocarbons as defined above, the following four bond-energy terms given in Table 1 are to be used for computation: $C^\phi \overline{\cdots} H$ (-6.80 kcal), $C^\phi \overline{\cdots} C^\phi$ (10.10 kcal), $C^\phi_* \overline{\cdots} C^\phi$ (7.03 kcal), and $C^\phi_* \overline{\cdots} C^\phi_*$ (1.53 kcal). These values have been derived from benzene and four other ultra-aromatics: naphthalene, phenanthrene, chrysene, and triphenylene. For every nonbenzenoid, aromatic sextet present in the polynuclear hydrocarbon, a correction term (2 kcal) due to the loss of some resonance energy in such a sextet must be used for compounds such as anthracene (with one nonbenzenoid sextet) or naphthacene (with two such sextets), etc. Such correction may not apply to "hydrogen-free" infinite networks such as graphite.

For subaromatic hydrocarbons, the aromatic portion of the molecule (containing the maximum possible benzenoid sextets) is first computed as in (1) above. For the rest of the molecule containing either a single bond or a double bond between two C^ϕ-carbons, the double bond is treated as $C^\phi \overline{\cdots} C^\phi$ (10.10 kcal) and the single bond as $C^\phi - C^\phi$ with -10.75 as the bond-energy term derived from biphenyl. For any methylene bridging between two aromatic moeties, the term $C^\phi - C^\phi$ is used.

For alkyl-, alkenyl-, and other similar "derivatives" of the basic aromatic moeties such as benzene and naphthalene, the corresponding group values for phenyl-, naphthyl-, etc. may be derived and used in place of the bondwise summation throughout. This is done by taking the computed $\Delta H_f^0(g)$ of the parent hydrocarbon from Table 4 and adding +6.8 kcal ($C^\phi \overline{\cdots} H$) per hydrogen atom replaced by the substituent side chain.

(D) Steric interactions in aromatics. Interactions not assignable to any particular bond but arising from a compound structural feature in the aromatic hydrocarbons are of the following types.

(1) Ortho-interaction. Two substituents in the ortho position of an aromatic moiety cause repulsive interactions which depend upon the size of the substituents. These contribute from +0.5 to +18 kcal to the heat of formation, shown in Table 1 as cis $[C^3 \ C^3]$ corrections.

(2) Trans-sextet interactions. Another kind of steric hindrance occurs when small substituents (a hydrogen or a methyl group) buttressed on bulky aromatic moieties are structurally juxtaposed. These interaction energy terms are given as trans-sextet [xxx] corrections in Table 1. An example of such interaction due to two interacting hydrogens is provided in the structure of 3,4-benzophenanthracene, the heat of formation of which is about 7 kcal more positive than a value calculated on the basis of primary aromatic bonds described under (A), (B), and (C). Similar inter-actions from two methyl groups (C_1^3), situated in critical positions of the aromatic structures, range up to 18 kcal as seen from the work of Frisch et al. [64]. However, the corresponding energy terms given in Table 1 are only approximate, derived from this datum and another [100].

(3) beta-Substitution. The substitution on beta carbon atoms of aromatic structure appears to be 0.2 kcal more stable (−) than alpha-substitution as seen from very precise (though singular) calorimetric work of Speros and Rossini [65] on methyl naphthalenes.

DISCUSSION OF RESULTS

The petroleum and petrochemical industry (especially in the United States) has given great impetus to hydrocarbon thermochemistry during the past three decades. Modern chemical technology involved in this industry required accurate enthalpies of formation and other thermody-namic data for the calculation of equilibrium constants of hydrocarbon reactions. Due to the ever-increasing demand after World War II for basic hydrocarbons such as benzene and toluene and aviation gasoline, and also for hydrocarbon monomers to meet the needs of the burgeoning plastics and synthetic rubber industries, considerable endeavor has been directed toward the determination of enthalpies and other thermodynamic and spectroscopic data of hydrocarbons. Much of the experimental data tabulated in this work is owed to such endeavor of the American Petroleum Institute in the extensive program on hydrocarbons pioneered by Rossini-Pitzer and co-workers. This monumental thermochemical work of the API

has not only benefitted the petrochemical industry immensely, but has also created an invaluable foundation to support theoretical organic chemistry by promoting similar work on other classes of organic compounds, thereby quantifying such concepts as resonance energy, steric hindrance, and conformational energy and ultimately the energy and nature of chemical bonds. In the past decade the science of thermochemistry and thermodynamics has been greatly accelerated by the constant search of space technology for high-energy rocket fuels and high-temperature resistant ablative materials.

The number of polyatomic hydrocarbon molecules that can be constructed with only two elements, tetravalent carbon and univalent hydrogen, is clearly very large, and with a few more common atoms, O, N, S, halogens, etc., the resulting number of possible organic compounds becomes astronomical indeed. It is clearly a hopeless task to expect to have tabulated, experimental thermochemical data (the heat of formation in the present context) on all such conceivable organic structure, or even on the restricted number of known compounds. It appears that with the help of the modern computer such thermodynamic information on a vast number of organic compounds can be handled, stored, and retrieved in the form of printouts. A recent 800-page volume on organic compounds by Stull, Westrum, and Sinke [19] is an example of such a computer approach to this problem. However, it is still impossible for any computer to give an estimate of properties for new compounds by merely storing such data on already measured compounds, however enormous the data. It is here that the bond-energy and group-contribution correlations play their important and indispensable role. A good bond-energy scheme providing for an adequate number and type of bonds, together with information precisely derived from a large body of known experimental data, will, once documented (perhaps in a computer), not only be capable of predicting the related property for any known, unknown, or hypothetical molecular structure, but can save all the labor of tabulating the experimentally observed data also. With this specific objective of developing a very elaborate and comprehensive scheme, no matter what large number of energy terms has to be worked out and documented, a large body of available experimental data on hydrocarbons have been employed to derive the various bond-energy terms numbering about 48 bond-energies + 24 correction terms + about 20 ring-strain terms to follow in Part III of this series. In this process no experimental data has been saved for the purpose of "prediction and comparison" to test the efficacy of the scheme, which must await new experimental thermochemical work in the future. For the time being, the over-all standard deviation of the error, $\Delta\Delta$ (obsd-calcd), should suffice equally well as a measure of success of the scheme developed. As seen from the computed figures at the end

of the Tables 2 to 5, the confidence limits (twice the standard deviation) of the heats of formation calculated by the new procedure are actually better than those of the experimental work on alkanes (Part I), alkenes, alkadienes, and alkynes. For aromatics, however, due to the lack of accurate data on heats of sublimation of many polycyclic aromatics and also some doubts about the purity of hydrocarbons used for combustion in some earlier work, the precision of the new method appears to have fallen, but is still not below ±1 kcal/mole for the whole wide range of aromatic compounds numbering about 100. Many other previous group-contribution and other methods tested in this manner on a large body of experimental data were seen to be much less precise than their claims, as shown in Part I. Only two of the best previous methods have been extended to this work, and comparison is made in Table 1 by the calculated confidence limits.

An assessment of the various existing methods as good standards for predicting $\Delta H_f^0(g)$ has been made recently (1969) by Gold [14], who after examing a large number of organic compounds (about 70 hydrocarbons and 106 other organic compounds) concluded that the precision of the best method for hydrocarbons, the Souders-Matthews-Hurd method (already analyzed critically in Part I) was ±3kcal/mole and for the method of Franklin [20], recommended by Gold as the best method for general organic compounds, was around ±6kcal/mole. The Franklin method is actually the most popular one used by many theoretical organic chemists (60-62, 67, 80) for the purpose of any quantitative discussion of resonance or strain energies. The error analysis of this method, made with extensive data in Tables 2 to 5, shows that it deviates in many cases by as much as ±20 kcal due to the inadequacy of bond-energy terms and the absence of many correction terms for both resonance and steric hindrance. Since much of the recent significant experimental thermochemical data was not available then, it is not surprising that the bond-energy terms and corrections lacking were not conceived of at the time of development of this method in 1949. This remark also applies to yet another method based on bondwise energy terms similar to our method and developed by Offtermatt in 1953. It has a precision of about ±11 to 18 kcal as evaluated by Gold [14]. Many other methods for alkanes have already been dealt with in Part I of this work where the high precision of the present method was established. The same general preacision has been nearly maintained when the method is extended to other hydrocarbons in this work, excepting some aromatics with rather imprecise experimental values of $\Delta H_f^0(g)$.

One major drawback of the procedure developed is the large number of

energy terms and correction terms, i.e., the parameters of the method. This was found inevitable, however, due to the very nature of "individuality" of every molecule, first in respect to covalent bonds with various energies and hybridizations, and second in respect to intramolecular nonbonding repulsive interactions (van der Waals' type) also specific to the molecule. Only in a few instances are the bonding and repelling forces in one molecule duplicated exactly in another. Therefore, a standard deviation, however small, is always to be expected in the calculated values, being inversely proportional to the number of parameters invoked. Tatevskii and Yarovoi [94], with their rigorous combinatorial analysis of the number and types of bonds between carbon atoms only, have found that there must be at least 9 C–C-type bond energy terms to cover all variations in alkane isomers, and some 23 types of C–C bonds to cope with higher alkenes. This analysis was made on the assumption that the C–H bonds in all hydrocarbons are identical in energy which, if it were not so, would entail many more terms. In Part I we have shown that the Tatevskii scheme, as formulated above for alkanes, still lacked a few more steric interaction terms without which the precision was totally lost for certain alkanes and polymers with the polyisobutylene-type 1,3-interaction. It is believed that in the present method a good compromise between precision and minimization of parameters has been achieved. In the most recent group-contribution method published by Benson and co-workers [31], the number of parameters (i.e., energy terms) are also quite large inevitably, and the attending over-all precision even somewhat smaller. In spite of having so many energy terms associated with it, the present bond-energy scheme does not claim the absolute completeness of its parameters in respect of either the number and type of bonds, or the interaction terms, so as to embrace all structural situations in the molecule, real or hypothetical. More terms may be added to the scheme when new experimental thermochemical data on compounds with yet-unencountered structural features (for example, $C^1-C_4^3$ bond) appear and warrant such addendum.

The incidence of a large number of bond-energy terms in this scheme is due to the fact that, as far as possible, all special structural effects causing either an increase or a decrease in bonding energy have been ascribed to some bond or other in the molecule, typified as a characteristic new bond and a new energy term attached to it. Thus, the conjugation energy in molecules like butadiene or butadiyne is assigned to C^2-C^2 and C^1-C^1 bonds with typical energy terms. Similarly, a positive energy balance due to steric hindrance, for example between two tertiary butyl groups joined by a single bond, has been ascribed to the bond designated as $C_4^3-C_4^3$,

with its bond energy lowered by an equivalent average steric energy. This norm in the new bond-energy scheme is in perfect accord with the theoretically well-founded hypothesis of Dewar and Schmeising [10], also followed by Cox [11], McGinn [13], and Bernstein [12] in their bond-energy schemes, that the lengths and hence energies of C—C and C—H bonds in hydrocarbons depend very largely on the state of hybridization of the carbon atom, giving rise to characteristic bond-energy terms preferably calculated at $0^0 K$. The concept of the bond energy of various hybridization states varying systematically with the bond lengths originated with Pauling [95], who proposed a relationship in which bond energy was proportional to the reciprocal of the equilibrium bond distance. Jenkin [96] favored the reciprocal of the square of bond length; while Glockler [90] expressed bond energies as a power series of the interatomic distance. Feilchenfeld [91], in an attempt to find a simpler relationship, originally chose the reciprocal-type of relationship like that of Pauling, but thought that the best power for the bond-length L was not the first [95], nor the second [96], but the third as in the relationship $E^0 = k(L)^{-3}$, with two k-parameters evaluated separately for C—C and C—H bonds. A linear first-order relationship for the C—H bond and a rather complex, nonlinear one for the C—C bonds were proposed by Bernstein [12] in his bond-energy scheme which is similar to ours but somewhat less elaborate and less rigorously tested as to the number of hydrocarbons. Finally, Dewar and Schmeising [10] advocated complex, two-parameter "tractrix" equations in bond length and bond energy for C—H and C—C bonds, fulfilling the necessary quantum-mechanical conditions of the bonding molecular orbitals. They proposed a number of independent bond-energy terms calculated from the observed bond lengths from x-ray and electron-diffraction data. The over-all agreement of this quasitheoretical bond-energy scheme, when tested extensively, is only around ±2 to 3 kcal, but the principle established is valuable, namely the bond-length bond-energy relationship. Dewar and co-workers have further elaborated their scheme in a very recent work [92] of SCF-Molecular Orbital calculations (the MINDO-method) which gives bond energies from observed or assumed molecular geometries. Although not a priori calculations owing to the use of empirically fitting parametric functions rather than absolute atomic orbitals, nor with results any better than ±2 kcal/mole, the procedure establishes theoretically the energy-geometry relationship of the chemical bond in general, and also for atoms other than carbon and hydrogen.

   In their earlier work Dewar and Schmeising [10] showed that absolute and unambiguous bond energies cannot be derived from any observed data

on heats of formation merely because it becomes mathematically unformid-able to solve the resulting set of simultaneous bond-energy vs. bond-type equations. Some energy terms (at least one per independent equation) have to be assumed to derive others analytically. As mentioned earlier, for this reason we have assumed the energies of all carbon-hydrogen bonds in order to derive those of carbon-carbon bonds, as both could not have been ob-tained simultaneously. The values of the former are well established and realistic (i.e., as they actually exist in the hydrocarbon, judged from the correlation of experimental bond dissociation energies and the total heat of atomization of the molecule [70, 97]). These C—H energy terms have been derived and confirmed by many previous workers, particularly by Cox in his pioneering bond-energy scheme [11] which essentially is extended widely and intricately in this work. These absolute energies of the C—H bonds, when plotted against the bond lengths (last column of Table 1) taken from Sutton's compilation [87], show a perfect linear relationship as depicted in Fig. 1, satisfying the least-square equation:

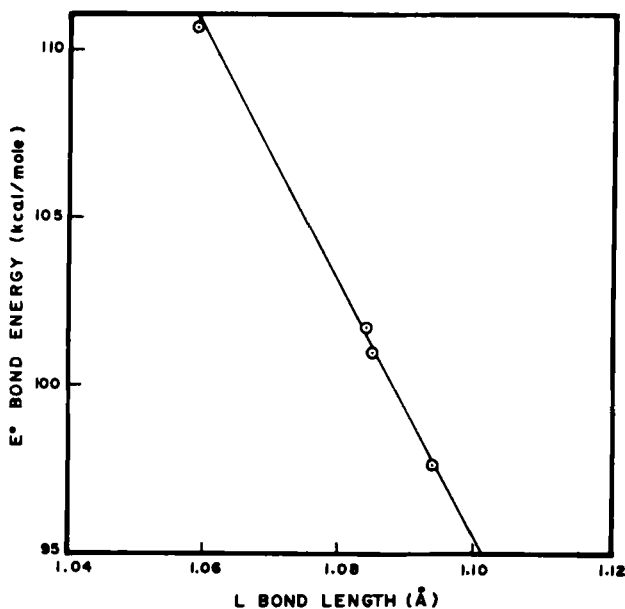$$E^0 = -372.230(L) + 504.945 \text{ kcal/mole} \qquad (1)$$

Fig. 1. Bond-energy bond-length relationship for the carbon-hydrogen bonds.

within a standard deviation of ±0.25 kcal/mole. The resulting C—C bond
energies (in all 16, covering a wide range from 85 to 170 kcal) were also
found to fit in a linear equation fairly closely as shown in Fig. 2. This is
in contrast to many complex relationships envisaged by previous workers
and summarized above. Since the bond energies in this work have been
derived from very extensive data, the result is considered significant. The
least-square equation for the carbon-carbon bond is

$$E^0 = -252.379(L) + 471.515 \text{ kcal/mole} \qquad (2)$$

with a standard deviation of ±2 kcal/mole.
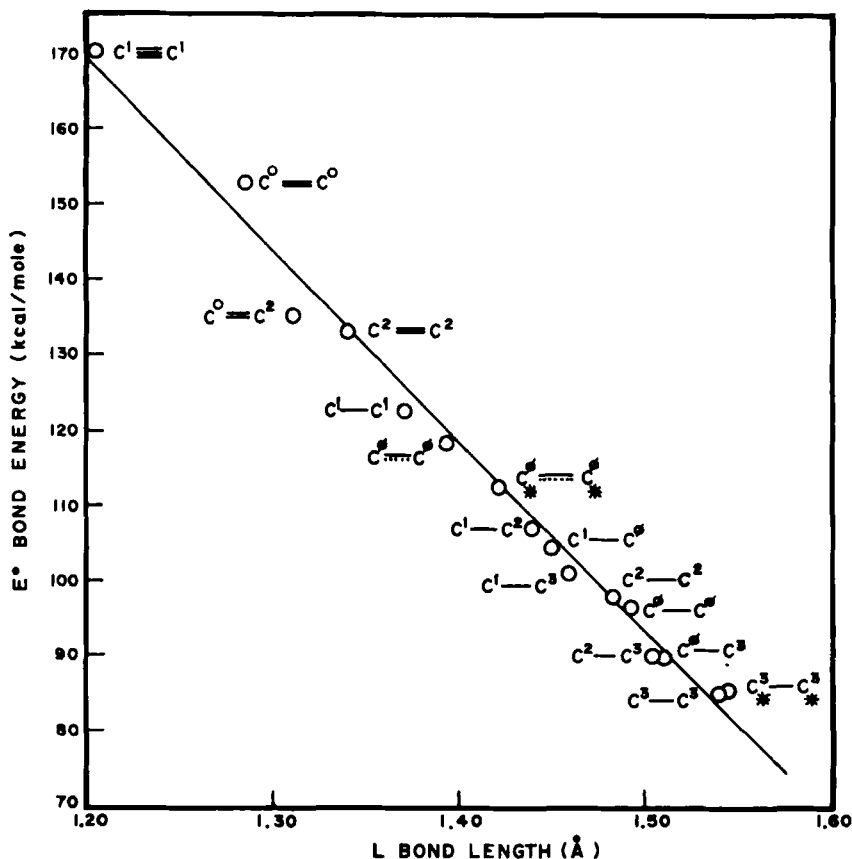
Fig. 2. Bond-energy bond-length relationship for the carbon-carbon bonds.

If an objective is set up to estimate the bonding energy (within ±2 kcal) from the molecular geometry only, like that of the SCF-MO calculations of Dewar [92], but purely empirically, the bond length is but one variable in the geometry of the bonding atoms; the other being the bond angle between a pair of bonds. Whereas the bond length is essentially related to the bonding energy (for which a satisfactory empirical relationship seems to have been obtained through Eqs. 1 and 2), the bond angles and their distortion are responsible for the strain (Baeyer strain) reducing the net bonding energy in the molecule. Evans [98], using thermochemical data on cycloalkanes and force constants, estimates the energy required to decrease the skeletal angle of the $(C^3-C^3-C^3)$ bond from the tetrahedral value of $109°28'$ by 5, 10, and 20°, to be only 0.4, 1.8, and 7 kcal, respectively. Assuming that the same energies apply to alter the bond angle (decrease or increase), it is clear that small angle distortions ($<10°$) are not very serious for the purpose of empirically estimating the bonding energy, except for small rings. There is, however, a third factor for which no additivity principle can ever apply very precisely. These are the nonbonded interactions (known as the Pitzer strain in reference to the cyclic hydrocarbons [80]) which must be calculated individually for every specific structure if precise values of conformational or strain energy are desired. The estimates of such strain correction terms given in Table 1 are only approximate. More precise calculations may be made in specific cases using complete molecular geometry and reliable potential functions for the van der Waals' interaction, as described, for instance, in the work of Pauncz and Ginsburg [99] on the calculation of strain energies and most stable conformations for medium-sized rings. However, for simple hydrocarbons with no severe strain energies of either Baeyer- or Pitzer-type, the practical value of our linear Eqs. (1) and (2) can be tested by calculating the heat of formation making use of bond lengths only, observed independently by other physical methods. Such a study is under way for hydrocarbons and will be extended to general organic compounds, if successful.

Table 5 shows the extension and applicability of the scheme to hydrocarbon polymers. The experimental data is sparse but in good agreement with the calculated values within ±0.25 kcal. A striking example of the accuracy of the bond-energy terms for aromatics is provided by graphite treated as a two-dimensional polymeric network interconnected by van der Waals "bonds" between the planes. The graphite structure is well known [95b] as a polycyclic array of aromatic bonds, with only two exo-double bonded carbons per sextet. The heat of formation in the gas phase, calculated by using the $C_*^\phi-C_*^\phi$ bond energy term (= 1.53 kcal) from Table 1,

is in excellent agreement with the observed value, numerically equal to the heat of sublimation of graphite, i.e., the lattice energy (2.26 kcal) determined experimentally from the heat of wetting [85]. The heat of formation of graphite in the crystalline state is zero by definition. Thus the scheme is universally applicable to small and large molecules alike, and heats of polymerization of hydrocarbon monomers as well as the enthalpies involved in the interconversion reactions of hydrocarbons, such as thermal cracking or simple isomerization, can be estimated at a single temperature (298°K) for the time being with a precision of ±0.5 kcal/mole. After full development of the scheme to cover halogens, oxygen, nitrogen and sulfur compounds, and a temperature range up to 1,000°K, it is hoped that the thermochemistry of all monomers and polymers can be handled without actual experimentation.

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