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 III. Alicyclic Hydrocarbons

R. M. Joshi[a]

[a] National Chemical Laboratory, Poona 8, India

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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 III. Alicyclic Hydrocarbons*

R. M. JOSHI

National Chemical Laboratory
Poona 8, India

ABSTRACT

The experimental data on the heats of formation of 137 monocyclic hydrocarbons and 44 polycyclic and cyclophane-type hydrocarbons have been analyzed, and strain-energy terms and empirical equations for monocyclic hydro-carbons derived to supplement the general bond-energy scheme developed for hydrocarbons. The over-all precision attained in predicting new values of heats of formation is of the order of ±1 kcal/mole, which is slightly poorer than the over-all uncertainty of ±0.8 kcal/mole in the available experimental data. The individual minimum energy conformation assumed by ring compounds is specific and somewhat defies the general additivity principle. This is more so for poly-cyclic nonaromatic hydrocarbons where deviations to

595

the extent of ±8 to 9 kcal/mole in the strain energy are
observed. The various factors responsible for strain in
ring compounds sometime either reinforce or reduce the
net strain energy. More elaborate procedures of com-
puting the strain energy of a ring structure are necessary
to evaluate the heat of formation precisely. Heats of
formation of some cyclic and polycyclic hydrocarbon
polymers are predicted for polycyclic repeat units by
using the group-contribution procedure.

INTRODUCTION

Strain-energy terms and empirical correlation equations for
computing the heats of formation of cyclic hydrocarbons containing
small, medium, and large rings have been developed to supplement
the general bond energy/group contribution scheme reported in
earlier work [1]. The appearance of a new monograph [2] in this
area, with exhaustive tabulation and critical selection of experi-
mental data on heats of formation and heats of vaporization, has
immensely facilitated the work of data collection. Similarly of
much help were the earlier review [3] and another valuable
treatise [13] on the subject. New experimental data from some
recent papers have been added. The over-all precision of ±1
kcal/mole attained in correlation in the present paper is appreci-
ably higher than that attainable by the recommended strain energy
terms and corrections in the previous work mentioned. The number
of new parameters (strain energy and other terms) introduced and
documented in this scheme is only 11, which is smaller than envis-
aged in other schemes. A vast amount of experimental data about
140 ring compounds has also been fitted in with the help of these
11 parameters. Polycyclic hydrocarbons are simply tabulated
and compared to the nearest calculated values, only to show that
an exact prediction of their heats of formation is beyond the
scope of the present additivity scheme based on transferability
of bond or group energies. For specific and precise calculation
of strain energy (also thermodynamic functions) of individual
molecular structures, a more sophisticated method employing
transferable valence-force potential functions and energy-
minimization procedure has recently become available [4].
    The reported polymerization and copolymerization of many
ring hydrocarbon monomers [5] such as cyclopropene and other

cycloolefins, norbornylene and other polycyclic hydrocarbons, and
the cyclopolymerization of dienes, has prompted the computation
of heats of formation of some of these polymers (Table 5). Heats
of polymerization of the corresponding monomers in the ideal gas
phase may be worked out in the usual manner, i.e., by the difference
($\Delta H_f°$, polymer - $\Delta H_f°$, monomer). No experimental values are yet
available on any of the polymers.

DERIVATION OF ENERGY TERMS

Table 1 lists the strain energy terms for various ring sizes
from three- to 17-membered rings. The $\Delta H_f°$(g)-contribution for
a strain-free structure is first calculated by making use of the
selected bond energy terms as listed in Table 2. The difference
between this value and the experimental value (converted to gas
phase by appropriate phase-change enthalpies) is attributed to
the ring strain, and averaged for a particular structure common
in a number of compounds. Wherever possible, empirical equa-
tions are formulated by trial and error for a typical pattern of
structural variation. The symbols used in Column 2 of Table 1
denote the cyclic structure, and Column 3 the energy term or
equation. Column 4 of this table gives the serial numbers of
compounds from which the energy term or equation was derived,
corresponding to Table 3. The types of carbon atoms forming
the ring structure are placed in square brackets, the subscript
number for the bracket denoting the ring size. Thus the symbol
"Cyclo$[C^2C^3]_3$" denotes a three-membered ring containing any
number of sp^2 and sp^3 carbon atoms totaling 3. l, m, and n are
a further classification of the carbon atoms as explained in the
footnotes to Table 1. The last symbol represents a special bond
energy term for a C—C bond between a sp^2 or an aromatic sp^ϕ
carbon and the cyclopropyl ring structure. Such a C^2—◁ bond
is found to be stabilized [to the magnitude of $\Delta H_f°$(g) = -7.0
kcal/mole] by an additional resonance energy effect [6] of about
2.7 kcal/mole over the general C^2-C^3 or $C^\phi-C^3$ bond, of magni-
tude -4.3 kcal/mole, in the open chain hydrocarbon.
    The selected energy terms for C—H and C—C bonds in Table 2
are those which fulfill the linear relationship in respect of
bond energy vs bond length as already shown in Part II [1].

TABLE 1. Strain Energy Correction/Correlation Terms for Monocyclic Hydrocarbons

No.	Structure	Strain energy (kcal/mole)[a]	Hydrocarbons from which derived	Remarks
1	$Cyclo[C^2C^3]_3$	$(27.4 + 13.3n) \pm 1.3$	1,2,4,5,10,11,13,14,25, 41,59,101	
2	$Cyclo[C^2C^3]_4$	$(26.4 + 1.9n) \pm 0.4$	3,6,12,15,23,28	
3	$Cyclo[C^2C^3]_5$	$(6.0 + 0.4m - 0.4 \, l) \pm 0.6$	7,8,16,20,21,22,26,27, 35-37,42-47,53,60,95, 99,101	
4	$Cyclo[C^2C^3]_6$	$(0.0 + n + 0.4m - 0.7 \, l) \pm 1.2$	18,24,29,38,39,48,54,55, 56,61,64-70,76,77,81-86, 92,93,96,98,100,106,117, 122,124-127	
5	$Cyclo[C^2C^3]_7$	$(5.4) \pm 0.7$	30,31,40,49,62,63,104	
6	$Cyclo[C^2C^3]_8$	$(9.6 - 2n) \pm 0.3$	51,57,71	$n = 2$ to 6 but not 8
7	$Cyclo[C^2C^3]_9$	$(12.5 - 1.5n)$	78,80	$n = 2$, single compound
8	$Cyclo[C^2C^3]_{10,11,14}$	$(11.6 - 3n)$	97,102,107,110,112	$n = 2$, single compound

9	Cyclo$[C^2C^3]_{12,13}$	$(4.4) \pm 0.5$	105,109	
10	Cyclo$[C^2C^3]_{15,16,17...}$	$(0.0) \pm 2.5$	116,118,119	
11	C^2 ▽	$(-7.0) \pm 0.4$ $E° = 92.6$ kcal/mole	(9),72,87,88,90,114	
	C^ϕ ▽			"Cyclopropyl resonance" [6] = 2.7 kcal/mole

[a] n = total number of C^2 carbons in the ring; m = number of exo-C^2 carbons; l = number of C^3 ring-carbons forming C^3—C bond outside the ring.

TABLE 2. Basic Bond-Energy Terms Used for Calculating $\Delta H_f°(g)$
of Molecular Structures without Strain-Energy Consideration
(taken from Part II, Ref. 1)

Bond	$\Delta H_f°(g)$ (kcal/mole)	Bond	$\Delta H_f°(g)$ (kcal/mole)
Carbon-Hydrogen Bonds		Carbon-Carbon Bonds	
C^3-H'	-1.78	C^3-C^3	0.45
C^3-H''	-2.68	C^2-C^3	-4.40
C^3-H'''	-3.48	$C^\phi-C^3$	-4.24
C^2-H'	-5.68	C^2-C^2	-12.97
C^2-H''	-6.38	C^2-C^ϕ	-10.75
$C^\phi\text{.....}H$	-6.80	$C^\phi-C^\phi$	-10.75
C^1-H	-15.75	C^1-C^3	-15.09
		C^1-C^2	-21.60
		C^1-C^ϕ	-18.83
		C^1-C^1	-36.83
		$C^\phi\text{.....}C^\phi$	10.10
		$C^\phi_*\text{....}C^\phi$	7.03
		$C^\phi_*\text{.....}C^\phi_*$	1.53
		$C^2=C^2$	38.00
		$C^0=C^2$	35.95
		$C^1\equiv C^1$	86.82

TABLE 3. Heats of Formation (Ideal Gas, 298.15°K) of Monocyclic Hydrocarbons

No.	Cyclohydrocarbon	$\Delta H_v°$ estimated[a] (kcal/ mole)	$\Delta H_f°(g)$ observed[b] (kcal/ mole)	$\Delta H_f°(g)$ estimated[c] without strain energy correction (kcal/ mole)	$\Delta H_f°(g)$ estimated (kcal/ mole)	Error $\Delta\Delta$ (kcal/ mole)	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	Cyclopropene		66.2 ± 0.6	12.48	66.5	-0.3	2
2	Cyclopropane		12.7 ± 0.2	-14.73	12.7	0.0	2
3	Cyclobutene		37.5 ± 0.4	7.57	37.8	-0.3	2
4	Methylenecyclopropane		48.2 ± 0.4	6.17	46.9	0.3	7
5	1-Methylcyclopropene		58.2 ± 0.3	3.32	57.3	0.9	2
6	Cyclobutane		6.8 ± 0.2	-19.64	6.8	0.0	2
7	Cyclopentadiene		31.9 ± 0.3	26.15	32.2	-0.2	2
8	Cyclopentene		8.2 ± 0.2	2.66	8.7	-0.5	2
9	Vinylcyclopropane	6.6	$(35.9 + 0.7)^d$	4.01	28.7	$(7.2)^d$	6
10	Ethylcyclopropane	6.8	$\underline{3.8 + 0.7}$	-26.05	1.3	2.5	2

(continued)

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TABLE 3 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
11	Ethylidenecyclopropane		38.5 ± 0.5	1.59	42.3	(3.8)	6
12	Methylenecyclobutane		29.2 ± 0.5	1.26	29.5	-0.3	8
13	Methylmethylenecyclopropane		39.9 ± 0.5	-0.24	40.5	-0.6	8
14	1,2-Dimethylcyclopropene		46.4 ± 1.5	-5.84	48.2	-1.8	8
15	1-Methylcyclobutene	6.4	28.3 + 0.5	-1.59	28.6	-0.3	8
16	Cyclopentane		-18.4 ± 0.2	-24.55	-18.6	0.2	2
17	Methylcyclobutane		-4.2 + 0.6	-26.05	0.3	-3.9	2
18	1,3-Cyclohexadiene		25.4 ± 0.2	21.24	25.2	0.2	2
19	1,4-Cyclohexadiene		25.1 ± 0.5	24.96	29.0	(-3.9)	3, 9
20	1-Methylcyclopentene		-0.6 ● 0.5	-6.50	-0.9	0.3	2
21	3-Methylcyclopentene		2.0 ± 0.5	-3.75	1.8	0.2	2
22	4-Methylcyclopentene		3.5 ± 0.5	-3.75	1.8	1.7	2
23	1-Methyl-3-methylenecyclo-butene		48.3 ± 0.5	15.59	47.7	0.6	3
24	Cyclohexene		1.1 ± 0.2	-2.25	-0.3	1.4	2
25	Bicyclopropyl		30.9 ± 0.9	-21.85	33.0	-2.1	2
26	Methylenecyclopentane	7.4	2.6 + 0.7	-3.65	2.7	-0.1	2

No.	Compound						
27	Methylcyclopentane		-25.3 ± 0.2	-30.96	-25.4	0.1	2
28	1,2-Dimethylcyclobutene		19.8 ± 2.0	-10.75	19.4	0.4	8
29	Cyclohexane		-29.5 + 0.2	-29.46	-29.5	0.0	2
30	1,3,5-Cycloheptatriene		43.9 ± 0.4	39.82	45.2	-1.3	2
31	1,3-Cycloheptadiene		22.6 ± 0.5	16.33	21.7	0.9	2
32	1,4-Cycloheptadiene			20.05	25.4	-	
33	1-Methylene-2-cyclohexene	8.3	(5.3 + 0.7)	14.93	18.3	(?)	2
34	1-Methyl-2-cyclohexadiene	8.2	(-5.8 ± 1.1)	14.83	18.1	(?)	2
35	1-Ethylcyclopentene	8.6	-5.3 ± 0.6	-11.41	-5.8	0.5	2
36	Vinylcyclopentane	8.4	0.1 ± 0.7	-5.81	-0.2	0.3	2
37	Ethylidenecyclopentane	8.8	-4.7 ± 0.7	-11.41	-5.0	0.3	2
38	1-Methylcyclohexene		-10.3 ± 0.2	-11.41	-10.1	-0.2	2
39	Methylenecyclohexane	8.5	-6.2 ± 1.0	-8.56	-7.2	1.0	2
40	Cycloheptene		-2.2 ± 0.2	-7.16	-1.8	-0.4	2
41	1,1-Dimethyl-2-ethylcyclo-propane	7.9	-13.7 ± 0.7	-40.67	-13.3	-0.4	2
42	1,1-Dimethylcyclopentane		-33.0 ± 0.3	-39.17	-33.1[f]	-0.1	2
43	1,2-Dimethylcyclopentane, cis		-31.0 ± 0.4	-37.37	-31.3	-0.3	2

(continued)

TABLE 3 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
44	1,2-Dimethylcyclopentane, trans		-32.7 ± 0.3	-37.37	-32.2	-0.5	2
45	1,3-Dimethylcyclopentane, cis		-32.5 ± 0.3	-37.37	-32.2	-0.3	2
46	1,3-Dimethylcyclopentane, trans		-31.9 ± 0.4	-37.37	-32.2	0.3	2
47	Ethylcyclopentane		-30.3 ± 0.3	-35.87	-30.3	0.0	2
48	Methylcyclohexane		-37.0 ± 0.3	-35.87	-36.6	0.4	2
49	Cycloheptane		-28.2 ± 0.2	-34.34	-28.9	0.7	2
50	Cyclooctatetraene		71.1 ± 0.3	54.68	54.68	(16.4)[j]	2
51	1,3,5-Cyclooctatriene		43.7 ± 1.5	45.63	43.2	0.5	2
52	Dimethylfulvene		32.1 ± 1.3	22.69	29.1	(3.0)	2
53	Allylcyclopentane	9.4	-6.4 ± 0.7	-10.72	5.1	-1.3	2
54	1-Ethylcyclohexene		-15.2 ± 0.3	-16.32	-15.0	-0.2	2
55	Ethylidenecyclohexane	9.5	-15.2 ± 0.6	-16.32	-14.9	-0.3	2
56	Vinylcyclohexane	9.5	-11.7 ± 0.6	-10.72	-11.4	-0.3	2
57	Cyclooctene, cis		-6.5 ± 0.3	-12.07	-6.5	0.0	2
58	Cyclooctene, trans		3.1 ±	-12.07	-6.5	(9.6)[j]	3

59	1,1-Dimethyl-2-propylcyclopropane	9.1	-18.6 ± 0.7	-45.58	-18.2	-0.4	2
60	n-Propylcyclopentane		-35.4 ± 0.3	-40.78	-35.2	-0.2	2
61	Ethylcyclohexane		-41.0 ± 0.4	-40.78	-41.5	0.5	2
62	Methylenecycloheptane		-8.2 ± 1.0	-13.47	-8.1	-0.1	3
63	1-Methylcycloheptene		-10.8 ± 1.0	-16.32	-10.9	0.1	10, 3
64	1,1-Dimethylcyclohexane		-43.2 ± 0.5	-45.86	-46.4[f]	3.2	2
65	1,2-Dimethylcyclohexane, cis		-41.1 ± 0.5	-42.28	-42.8	1.7	2
66	1,2-Dimethylcyclohexane, trans		-43.0 ± 0.5	-42.28	-43.7	0.7	2
67	1,3-Dimethylcyclohexane, cis		-44.1 ± 0.4	-42.28	-43.7	0.4	2
68	1,3-Dimethylcyclohexane, trans		-42.2 ± 0.4	-42.28	-43.7	1.5	2
69	1,4-Dimethylcyclohexane, cis		-42.2 ± 0.4	-42.28	-43.7	1.5	2
70	1,4-Dimethylcyclohexane, trans		-44.1 ± 0.4	-42.28	-43.7	-0.4	2
71	Cyclooctane		-29.7 ± 0.3	-39.28	-29.7	0.0	2
72	Phenylcyclopropane	11.7	36.4 ± 0.9	11.21	35.9	0.5	2
73	Indene		39.1 ± 0.4	35.29	40.5	-1.4	2

(continued)

TABLE 3 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
74	Indane		14.4 ± 0.5	9.74	14.9	-0.5	2
75	Cyclohexylcyclopropane	11.1	(-64.1 ± 1.2)d	-36.58	-9.9	(?)d	2, 6
76	n-Propylcyclohexane		-46.2 ± 0.3	-45.69	-46.4	-0.2	2
77	1,3,5-Trimethylcyclohexane, cis		-50.7 ± 0.4	-48.69	-50.8	0.1	2
78	Cyclononene, cis		-7.2 ± 1.0	-16.98	-7.5	0.3	3
79	Cyclononene, trans		-4.3 ± 1.0	-16.98	-7.5	(3.2)j	3
80	Cyclononane		-31.7 ± 0.4	-44.19	-31.7	0.0	2
81	1-Methyl-1-ethylcyclohexane	10.1	-47.3 ± 0.5	-48.99	-49.5f	2.2	11
82	1-Methyl-2-ethylcyclohexane, cis	10.6	-45.9 ± 0.5	-47.19	-47.7	1.8	11
83	1-Methyl-2-ethylcyclohexane, trans	10.4	-47.0 ± 0.5	-47.19	-48.6	1.6	11
84	1-Methyl-3-ethylcyclohexane, cis	10.6	-48.4 ± 0.5	-47.19	-48.6	0.2	11
85	1-Methyl-4-ethylcyclohexane, cis	10.6	-46.5 ● 0.5	-47.19	-48.6	2.1	11
86	1-Methyl-4-ethylcyclohexane, trans	10.4	-48.5 ± 0.5	-47.19	-48.6	0.1	11

87	2-Methyl-1-cyclopropyl-benzene	10.8	28.8 ± 0.7	3.33	28.9	-0.1	12
88	2,4-Dimethyl-1-cyclopropyl-benzene	12.0	20.7 ± 0.7	-4.55	21.0	-0.3	12
89	2,4,6-Trimethyl-1-cyclo-propylbenzene	13.2	14.5 ± 0.7	-12.43	14.1	0.4	12
90	4-Isopropyl-1-cyclopropyl-benzene	13.0	16.4 ± 0.7	-7.99	16.7	-0.3	12
91	1,1-Dimethyl-2-pentylcyclo-propane	11.3	-28.7 ± 1.0	-55.40	-28.0	-0.7	13
92	Azulene		73.5 ± 1.0	66.74	78.1	(-4.6)^h	2
93	1,2-Dihydronaphthalene	12.4	30.4 ± 1.7	30.38	31.0	-0.6	2
94	1,4-Dihydronaphthalene	12.4	33.4 ± 1.7	32.04	32.6	0.8	2
95	1,2,3,4-Tetrahydro-naphthalene		7.3 ± 1.2	4.83	3.4	(3.9)	2
96	Dicyclopentyl	11.7	-30.1 ± 0.8	-41.49	-30.3	0.2	2
97	n-Butylcyclohexane		-50.9 + 0.4	-50.60	-51.3	0.4	2
98	Cyclodecane		-36.9 + 0.4	-49.10	-37.5	0.6	2
99	1-Methyl-1,2,3,4-Tetra-hydronaphthalene	13.5	-2.7 ± 6.0	0.20	-1.9	-0.8	2
100	Dicyclopentylmethane	13.0	-36.0 ± 0.7	-46.40	-35.2	-0.8	2

(continued)

TABLE 3 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
101	Cyclopentylcyclohexane	12.4	-42.6 ± 1.2	-46.40	-41.5	-1.1	2
102	1,1-Dimethyl-2-hexylcyclo-propane	13.1	-33.0 ± 0.6	-60.31	-32.9	-0.1	2
103	Cyclo-undecane		-42.9 + 0.4	-54.01	-42.4	-0.5	2
104	Acenaphthylene		61.6 ± 1.2	54.59	61.8	-0.2	2
105	Cyclopentylcycloheptane	14.1	-40.0 ± 1.0	-51.31	-40.3	0.3	2
106	Cyclododecane		-55.0 ± 0.6	-58.92	-54.5	-0.5	2
107	n-Heptylcyclohexane		-68.9 ± 0.6	-65.33	-66.0	-2.9	2
108	Cyclodecene, cis		-15.7 ± 1.0	-21.44	-15.8	0.1	10
109	Cyclodecene, trans		-12.4 ± 1.0	-21.44	-15.8	$(3.4)^j$	10
110	Cyclotridecane		-58.9 ± 0.5	-63.83	-59.4	0.5	2
111	1,8-Cyclotetradecadiyne		75.0 ± 1.0	63.28	74.9	0.1	2
112	Dicycloheptyl	16.1	-52.0 ± 0.9	-61.13	50.3	-1.7	2
113	Cyclotetradecane		-57.1 ± 0.5	-68.74	-57.1	0.0	2
114	1,1-Diphenylcyclopropane	17.5	61.8 ± 1.0	35.35	61.4g	0.4	2
115	1,2-Diphenylcyclopropane, cis	17.8	60.5 ± 0.6	37.15	60.5g	0.0	2

116	1,2-Diphenylcyclopropane, trans	17.6	'57.3 ± 0.9	37.15	59.2	-1.9	2
117	Cyclopentadecane		-72.0 ± 0.5	-73.65	-73.7	1.7	2
118	n-Decylcyclohexane		-81.1 ± 0.5	-80.06	-80.8	-0.3	2
119	Cyclohexadecane		-76.9 ± 0.5	-78.56	-78.6	1.7	2
120	Cycloheptadecane		-87.1 ± 0.6	-83.47	-83.5	-3.6	2
121	Diphenylfulvene		(96.1 ± 4.0)	84.07	90.5	(5.6)	2
122	[18]-Annulene	31.1	(70.1 ± 5)	{ 123.03 / 59.54e	123.0 / 59.5	(-52.9)j / (10.6)e	2
123	n-Dodecylcyclohexane		-89.4 ± 0.9	-89.88	-90.6	1.2	2
124	11-Cyclopentylheneicosane	28.8	-126.2 ± 3.0	-130.66	-125.1	1.1	2
125	3-Cyclohexyleicosane	28.1	-131.1 ± 3.0	-130.66	-131.4	0.3	2
126	9-Cyclohexyleicosane	28.1	-133.0 ± 3.0	-130.66	-131.4	-1.6	2
127	11-Cyclohexylheneicosane	28.2	-136.6 ± 3.0	-135.57	-136.3	-0.3	2
128	13-Cyclohexylpentacosane	34.1	-155.3 ± 2.1	-155.21	-155.9	0.6	2
129	2-Cyclopropyl propene	7.6	-19.3 ± 1.0	-5.15	19.5	-0.2	13
130	2-Cyclopropyl propane	7.4	-3.7 ± 1.0	-32.46	-5.1	1.4	13
131	2-Cyclopropyl butane	8.6	-9.3 + 1.0	-37.37	-10.0	0.7	13
132	3-Vinylcyclohexene		(16.8 ± 3.0)l	10.02	11.3	(?)	17

(continued)

TABLE 3 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
133	Acenaphthene		37.4	30.70	37.9	-0.5	13, 2
134	1-Cyclopentyldecane		-69.8	-75.15	-69.6	-0.2	18
135	Cyclotriacontane	66	(-148)	-147.30	-147.3	-	13
136	+-Limonene		-1.5)	-1.83	-0.5	-1.0	2
137	Dipentene (+,-)		-0.6				
	Standard error		±0.8	±0.3		±1.0	
	Confidence limits		2.0	±0.5		±2.5	

a Heat of vaporization $\Delta H_v{}^\circ$ or heat of sublimation $\Delta H_v{}^\circ$, calculated by the method of Small [14] or of Bondi [16].

b Underlined figures in this column indicate that calculated values of $\Delta H_v{}^\circ$ or $\Delta H_v{}^\circ$ have been combined with the experimental $\Delta H_f{}^\circ$ for the condensed phase.

c Estimated by using selected bond energy/group contribution terms given in Table 2.

d The NBS measurements reported by Fierens and Nasielski [6] for the compound disagree with this or any other bond energy/group contribution correlation.

e Calculated using the terms for fully aromatic bonds as for naphthalene, see Part II [1].

f One cis $[C_1^3C_1^3]$ correction = 0.9 kcal/mole applied for 1,1-dimethyl substitution also.

g cis$[C^\phi C^\phi]$ correction for cyclopropane ring is assumed to be about 1.4 kcal/mole and applied to 1,1-disubstitution also.

h Resonance energy due to partial aromatization.

i Group contributory estimate of Duncan and Janz [17].

j See text.

Many other subtler energy terms which were devised for open-chain alkanes, alkenes, and alkadienes do not allow any better fit with the experimental data on alicyclic hydrocarbons than by use of the limited number of selected basic terms. This is mainly due to the aforesaid inherent specificity of every ring structure.

The heats of vaporization ΔH_v°, shown in Column 3 of Tables 3 and 4, have been calculated by the method of Small [14] to which many new terms have been added as arising from new experimental data available since its publication. The method is based on the hypothesis that the cohesive energy density should be an additive property for molecules, similar to the molar refraction or the parachor. It is thus a group contribution method requiring only the density (at 25°C) as the input data which, for hydrocarbons, is mainly drawn from Ref. 15, allowing a temperature correction of 0.001 per degree to the densities at 20°C given therein. The heat of sublimation, ΔH_v° required for a few compounds was calculated (and shown underlined) by the method of Bondi [16] which is also a group contribution type. Certain values of $\Delta H_f^\circ(g)$ observed in Column 4 of this table show abnormally large deviation from their calculated estimates in Column 6. Since no specific structural factor responsible is apparent in these molecules, the experimental data seem to be in error and such data have been shown in parenthesis. In computing the over-all standard error from the individual errors $\Delta\Delta$, ($\Delta H_f^\circ(g)$-observed - $\Delta H_f^\circ(g)$-calculated), certain other molecules have also been excluded where the large error is clearly attributable to a very special structural feature. Such a feature is hardly duplicated in any other molecule so as to warrant an energy term for it; for example, the special strain-relief in the 1,4-cyclohexadiene molecule caused by the removal of four interfering hydrogen atoms from the cyclohexane ring which is taken as strain free only in the chair conformation, for the purpose of this scheme.

The high strain energy of 16.4 kcal/mole in cyclooctatetraene, or the strain energies of trans-cyclo octene, trans-cyclononene, and trans-cyclodecene (9.6, 3.2, and 3.4 kcal/mole, respectively), azulene, and [18]-annulene are also such special cases with high error and are excluded from the over-all standard error. $\Delta H_f^\circ(g)$ of 3-vinylcyclohexene is yet another case where the experimental value from a equilibrium study of the dimerization of butadiene seriously conflicts with the calculated value [17]. The $\Delta H_f^\circ(g)$ of [18]-annulene, when calculated by using aromatic bond-energy terms, comes closer to the experimental value,

leaving a reasonable margin of 10.6 kcal/mole as the strain energy
for this 18-membered ring with alternate C^2-carbons. [18]-Annulene
thus appears to be an essentially aromatic structure with a net reso-
nance energy of 53 kcal/mole (overcoming ring strain), as judged
from its disagreement when ordinary energy term for the C^2-C^3
conjugated bond are used. [18]-Annulene fulfills the well-known
condition for aromaticity; namely, a (4n + 2), out-of-plane,
π-electron system.

DISCUSSION

In cyclic hydrocarbons one must recognize at least two distinct
types of strain energy; the first, caused by distortion of bond angles
and encroachment of normal bond distances designated as the
"Bayer strain" (B-strain), and the second, due to the nonbonded
repulsive interactions of hydrogens in their partially eclipsed
(gauche) or totally eclipsed (cis) positions, known as the "Pitzer
strain" (P-strain). In small rings (n = 3, 4) the B-strain plays a
dominant role, with its magnitude enormously high compared to
the other kind of strain. In five-membered rings the bond angles
and distances are only slightly distorted, if at all, from the normal,
and B-strain is essentially absent but the P-strain begins to show
its effect. It is to be noted that P-strain is dependent essentially
upon the number of interacting hydrogens (or halogens, in case of
halocarbons) attached to the ring atoms. If, in a ring, a C^3 carbon
is replaced by a C^2, the B-strain may rise due to a possible angle
distortion, especially in small rings, but the P-strain is reduced
at the same time because of the lesser number of interfering
hydrogens. One finds an interesting compromise of these opposing
strain factors in the five-membered carbon ring where progressive
replacement of C^3 by C^2 carbons has little effect on the strain
energy of the molecule, the mean value being 6.0 ± 0.6 kcal/mole,
as seen from the equation for five-membered rings in Table 1.
However, in the four-membered ring such replacement seems to
increase the over-all ring strain by approximately 1.9 kcal/mole
per C^2 carbon introduced, and in the three-membered ring by as
high as 13.3 kcal/mole per C^2 carbon, P-strain changes being
relatively insignificant. The introduction of an exo-C^2 carbon in
five- and six-membered rings seems to cause an excess strain
of about 0.4 kcal/mole over an ordinary C^2 within the ring as
expressed in the empirical equations developed for the five- and

six-membered rings. In seven-membered and larger rings, very little bond angle distortion is caused by a C^2 carbon replacing a C^3 except in the cases of the trans placement of the C^2-C^3 bonds as in trans-cyclooctene when B-strain becomes significant again. The strain factor of such trans placement decreases progressively in larger rings such as trans-cyclononene and decene.

In a simple six-membered ring with all C_2^3 carbons, viz., cyclohexane, the B-strain is essentially zero for the carbon skeleton and the P-strain is also reduced to a minimum in the "chair" conformation of the molecule with completely staggered (trans) hydrogens. The basic bond energy terms evolved in this work for the C^3-C^3 and C^3-H'' bonds are such that they predict a normal heat of formation for cyclohexane, i.e., with a minimal (zero) strain energy, making it (the chair form) the reference point for cyclic hydrocarbons. However, the replacement of C_2^3 in cyclohexane or in cyclopentane by a tertiary or a quaternary carbon (C_3^3 or C_4^3) carbon as in substituted cycloalkanes, the P-strain is further reduced below zero by about 0.4 to 0.7 kcal/mole per hydrogen atom replaced as in alkyl cyclohexanes or cyclopentanes. This correlation is incorporated in the empirical equations in Table 1.

It is well known that nonbonded atoms attract each other at large interatomic distances and repel each other at very short distances (between 2 and 3 Å). It seems reasonable that such forces exist universally between nonbonded atoms of the same molecule as well as between those of different molecules. The interaction energy is a function of distance. A variety of such potential energy functions for interactions between nonbonded atoms has been proposed in connection with computing barriers to internal rotation. These have been reviewed by Cignitto and Allen [19]. The maximum H...H repulsion energy in their totally eclipsed position has been calculated by various methods and workers to a modest agreement of 1.34 to 2.46 kcal/mole [20]. Therefore, in simple cycloalkanes with all C_2^3 carbons, one such repulsion interaction of a juxtaposed hydrogen pair may cause a maximum strain energy of 2.5 kcal/mole in an extremely unfavorable position. In the less severe cases of cyclopentanes and cyclohexanes, the repulsion energy ranges from 0.8 to 1.4 kcal/mole only.

Courtauld molecular models show that in a five-membered cyclopentane ring the B-strain is zero for a planer structure, but in this conformation (symmetry: C_{2v}) all five pairs of

hydrogens become eclipsed almost perfectly, so that the P-strain
of such structure would exceed 10 kcal/mole. Cyclopentane there-
fore assumes a nonplanar conformation (symmetry: C_s, due to any
one of the five carbons being out-of-plane in succession, known as
the "pseudorotation") at the expense of causing some B-strain.
This has been confirmed by Pitzer [28] from spectroscopic cal-
culation of entropy and the experimental specific heat data. A net
strain energy thus minimized to about 6 kcal/mole prevails over
the nonplanar cyclopentane molecule. Cyclopentadiene, on the
other hand, has a planar conformation but no P-strain owing to
the reduced number of interfering hydrogens; the B-strain has,
however, increased due to the four out of five sp^2-hybridized
carbons, giving again a net strain energy of about 6 kcal/mole.
The B-strain in five-membered ring seems to rise to the maxi-
mum of about 9 to 10 kcal/mole when all carbon atoms are C^2,
as seen from the strain energy of dimethyl or diphenyl fulvenes.
Due to the specific nature of the over-all strain energies in
alicyclic hydrocarbons, depending upon the particular conforma-
tion which the molecule assumes to minimize its potential energy,
the general bond energy scheme developed in this work has not
attained the same high precision as in the previous correlation
on open chain or aromatic hydrocarbons. Only a limited number
of strain energy terms and empirical equations of general appli-
cation have been incorporated in the scheme as shown in Table 1.

cis-trans Energy Corrections

In open chain alkenes the trans isomer is always regarded as
having the lower steric hindrance and lower energy, i.e., $\Delta H_f°(g)$
more negative. This is no longer the case with cycloalkanes. The
experimental $\Delta H_f°(g)$ values of dimethylcyclopentanes and dimethyl-
cyclohexanes (Nos. 43-46 and 65-70 in Table 3) show that in
1,2-disubstituted cycloalkanes in general the trans isomer is
energetically lower. It is also lower in the case of 1,4-disubstituted
cyclohexanes and reasonably for more distant dimethyl substitution
in higher cycloalkanes as well. However, in both 1,3-dimethyl-
cyclopentane and cyclohexane the cis isomer has a lower steric
hindrance and a more negative heat of formation. The average
magnitude of this effect is about 1.5 kcal/mole for 1,2- and
1,4-disubstitutions and about 0.5 kcal/mole for 1,3-disubstitution.
The sign of this energy correction is, however, solely determined

by individual molecular model study. For the purpose of this scheme, we have used 0.9 kcal/mole throughout as the cis-trans correction, which is an earlier derived term for such effect in the open-chain alkanes [1]. This correction term is applied only to 1,2-dimethyl and 1,1-dimethylcycloalkenes where the repelling methyl groups are on the same or adjacent carbon atoms.

Regarding cis-trans isomers with respect to the double bond as in cycloalkenes, a stable (to exist) trans isomer first appears in an eight-membered ring, which becomes more stable in nine- and 10-membered cycloalkenes and may eventually become stabler than the cis in larger rings, as per convention in the open-chain alkenes. A triple bond in the ring first appears in cyclooctyne, though highly strained, but cyclononyne is essentially strain free. The smallest cyclic allene so far prepared is 1,2-cyclononadiene, but cyclic allenes seem to be less strained than the corresponding acetylenic isomers, as judged from the reported stability in preparative chemistry and in the absence of any thermochemical data on either cyclic allenes or acetylenes.

trans-Annular Strain

This type of P-strain is caused by interactions of substituents (or merely hydrogens) on the ring atoms which are diametrically opposite, or nearly so, in the ring whose internal space is not large enough for all quasi-axial hydrogen atoms to fit without causing some compression of the normal van der Waal radii of the hydrogens. The cyclic molecule endeavors to minimize this strain energy also, along with the minimization of B-strain, by assuming a conformation which is a compromise between these two factors. In seven- to 11-carbon containing rings, any conformation in which all bonds are gauche contains a trans-annular strain progressively increasing with the ring size and accounts for the rising strain energy from the seven- to the 11-membered cycloalkane. Cyclotetradecane (C-14) has an anomalously high strain of 11.6 kcal/mole, which is 7 kcal higher than either C-12 or C-13 cyclane and does not fit in with the trend of decreasing strain energy in large rings up to the 17-membered, confirmed by the precise experimental values available. Experimental confirmation is perhaps needed for C-14 datum since molecular model study does not also reveal any special cause for such high strain in C-14.

Polycyclo- and Spirohydrocarbons and Cyclophanes

In Table 4, Column 5, are given the basic binding energies of polycyclic hydrocarbon skeletons, and in Column 6, the net strain energy in the polycyclic structure. The calculated $\Delta H_f°(g)$ values in Column 7 take into account the sum of the strain energies of component monocyclic rings, yet they largely disagree with the experimentally observed values in Column 4. The error in some cases is as high as 21 kcal/mole and it averages around 8 to 9 kcal/mole, indicating a failure of the assumption of additivity of component ring strains in polycyclanes. The conformations of the fused rings will, in general, be different from the separate rings. The H...H tortional interactions (P-strain) would be reduced in the fused systems but the bond angles and distances are affected so as to raise the B-strain. Since these factors are compensatory, the additivity principle of component ring strains sometimes seems to work very well (but only fortuitously) for many polycyclo hydrocarbons, even for some notably complex structures like cubane (No. 13 in Table 4) or hexacyclo-[...]dodecane (No. 30 in Table 4). The total strain energy in a multiple ring system must be calculated on a more fundamental basis, taking into account the individual molecular geometry, the potential functions determined by force constants for stretching, bending and twisting modes of the bonds, the nonbonding interactions, and by an iterative procedure of minimization of molecular energy as described by Boyd and co-workers [4].

Polymers

Several polymer structures and the calculated heats of formation are depicted in Table 5. For polymers with polycyclic repeat units (e.g., Nos. 11, 15, and 21), the group contribution of the basic polycyclic moiety, a "diradical," is worked out from the corresponding experimental $\Delta H_f°(g)$ of the polycyclic molecule and the bond energies of two C—H bonds that are eliminated in the polymer by a C—C polymer link. As observed from the reviews [5] of Ketley and Fisher, and Minoura, these polymers are actually encountered in the polymerization of cyclic hydrocarbons and dienes by ionic and metal-complex catalysts. It is seen that most of the postulated polymerization mechanisms are energetically feasible since the heats of formation of the resulting polymers are appreciably more negative than the respective monomers. A relative idea of the stabilities of various polymer structures can be had from the present study.

TABLE 4. Heats of Formation (Ideal Gas, 298.15°K) of Polycyclic and Spiro Hydrocarbons and Cyclophanes

No.	Hydrocarbon	ΔH_v° (kcal/ mole)	ΔH_f°(g) observed (kcal/mole)	ΔH_f°(g) calculated without strain energy correction (kcal/ mole)	Strain energy (kcal/ mole)	ΔH_f°(g) calcu- lated (kcal/ mole)	Error $\Delta\Delta$ (kcal/ mole)	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Polycyclic Hydrocarbons							
1	Bicyclo[1,1,0]butane		51.9 ± 0.2	-12.03	63.9	42.8	9.1	3
2	Bicyclo[2,1,0]pentane		37.6 ± 2.0	-16.94	54.4	36.9	0.7	3, 8
3	1,3-Dimethyl[1,1,0]butane		(39.7 ± 2.0)	-28.45	68.2	26.3	13.4	3, 8
4	cis-Bicyclo[3,1,0]hexane		9.3 ± 0.8	-21.85	31.2	10.7	-1.4	4
5	Bicyclo[2,2,1]hepta-2,5-diene	7.7	55.7 ± 2.0	27.66	29.5	38.7	17.0	8, 25
6	Bicyclo[2,2,1]hept-2-ene		20.9 ± 2.0	0.5	20.4	10.5	10.4	8, 25

(continued)

TABLE 4 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
7	cis-Bicyclo[4,1,0]heptane		0.4 ± 1.0	-26.76	27.2	-0.8	1.2	4
8	Bibyclo[2,2,1,]heptane	9.8	-12.2 ± 0.7	-26.76	14.6	-17.3	5.1	2
9	Bicyclo[2,2,2]octa-2,5,7-triene, "Barrelene"		72.7 ± 2.0	49.96	22.7	51.2	21.5	8
10	Bicyclo[2,2,2]octa-2,5-diene		33.4 ± 2.0	22.75	10.6	22.6	10.8	8
11	Bicyclo[4,2,0]octa-2,4-diene		45.5 ± 2.0	19.03	26.5	44.8	0.7	23
12	Bicyclo[2,2,2]oct-2-ene	10.9	5.6 ± 1.0	4.46	1.1	2.3	3.3	2
13	Tricyclo[3,3,3]octane, "Cubane"		148.7 ± 1.0	-8.84	157.5	149.6	-0.9	2
14	cis-Bicyclo[5,1,0]octane		-3.8 ± 0.7	-31.67	27.9	1.1	-4.9	4
15	cis-Bicyclo[4,2,0]octane		-6.1 ± 1.0	-31.67	25.6	-6.7	0.6	4
16	cis-Bicyclo[3,3,0]octane		-22.3 ± 0.5	-31.67	9.4	-21.3	-1.0	4
17	trans-Bicyclo[3,3,0]octane		-15.9 ± 0.6	-31.67	15.8	-21.3	5.4	4
18	Bicyclo[2,2,2]octane	12.3	-22.8 ± 1.0	-31.67	8.9	-34.5	11.7	2
19	Bicyclo[3,3,1]non-1-ene		(-0.5 ± 1.0)	-12.12	12.0	-12.5	12.0	24
20	cis-Bicyclo[6,1,0]nonane		-7.6 ± 1.0	-36.58	29.0	0.4	-8.0	4

21	cis-Bicyclo[4,3,0]nonane, "cis-Hydrindan"	-30.4 ± 0.5	-36.58	6.2	-32.8	2.4	21, 4
22	trans-Bicyclo[4,3,0]nonane, "trans-Hydrindan"	-31.4 ± 0.5	-36.58	5.2	-32.8	1.4	21, 4
23	cis-Bicyclo[5,3,0]decane	-31.1 ± 1.2	-41.49	10.4	-30.9	-0.2	4
24	trans-Bicyclo[5,3,0]decane	-31.4 ± 2.0	-41.49	10.1	-30.9	-0.5	4
25	cis-Bicyclo[4,4,0]decane, "cis-Decalin"	-40.5 ± 0.6	-41.49	1.0	-44.3	3.8	22, 4
26	trans-Bicyclo[4,4,0]decane "trans-Decalin"	-43.5 ± 0.6	-41.49	-2.0	-44.3	0.8	22, 4
27	1,3,5-Trimethylbicyclo[3,1,0]hexane	(-15.5 ± 2.0)	-41.08	25.6	-8.9	(-6.6)	27
28	Tricyclo[2,2,1,0^{2,6}]heptane, "Nortricyclane"	23.8 ± 2.0	-19.15	43.0	22.6	1.2	8
29	Quadricyclo[2,2,1,0^{3,5}]heptane "Quadricyclane"	83.6 ± 2.0	-7.96	91.6	82.0	1.6	8
30	Hexacyclo[7,2,1,0^{2,5},0^{4,8},0^{6,12}]dodecane	24.0 ± 2	-20.87	44.9	23.1	0.9	27
31	α-Pinene	6.8 ± 0.6	32.32	25.5	3.1	3.7	2
32	β-Pinene	9.3 ± 0.8	32.32	23.0	5.9	3.4	2

(continued)

TABLE 4 (continued)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	Spiro Hydrocarbons							
33	Spiro[2,2]pentane		44.3 ± 0.2	-18.74	63.0	63.0	8.2	2
34	Spiro[4,4]nonane	10.4	-24.0 ± 0.6	-38.38	14.4	-28.0	4.0	2
35	Spiro[4,5]decane	11.6	-36.3 ± 0.6	-43.29	7.0	-39.5	3.2	2
36	Spiro[5,5]undecane	12.8	-46.5 ± 0.6	-48.20	1.7	-51.0	4.5	2
37	Spiro[5,6]dodecane	14.0	-46.5 ± 0.6	-53.11	6.6	-49.1	2.6	2
	Cyclophanes							
38	2,2-para-Cyclophane		59.9 ± 1.9	29.30	30.6	40.9[a]	19.0	26
39	2,2-meta-Cyclophane		40.7 ± 1.9	29.30	11.5	40.9[a]	0.2	2
40	2,2-meta-para-Cyclophane		52.2 ± 0.7	29.30	22.9	40.9[a]	11.3	26
41	2,2-Perhydro-paracyclo-phane		-37.4 ± 3.6	-63.34	25.9	-58.9[a]	21.5	2
42	3,3-para-Cyclophane		30.9 ± 0.9	19.48	11.4	23.9[a]	27.0	2
43	1,8-para-Cyclophane		6.9 ± 2.2	4.75	2.1	4.8	2.1	26
44	6,6-para-Cyclophane		-18.5 ± 2.8	-9.98	8.5	-10.0	8.5	26
	Standard error		±1.5	-	-	-	±8.6	
	Confidence limits		3.0				17.0	

[a]Assuming basic strain energy correction of the respective cycloalkane with appropriate number

TABLE 5

HEATS OF FORMATION $\left[\Delta H_f^{\circ}\,(g)\right]$ OF SOME

CYCLIC MONOMERS AND POLYMERS [a]
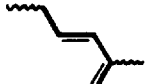
NO	MONOMER	POLYMER
1	CYCLOPROPENE (C_3H_4) 66.2	(20.3) trans : 12.5 cis : (13.4)
2	CYCLOPROPANE (C_3H_6) 12.7	(− 14.7)
3	CYCLOBUTENE (C_4H_6) 37.5	(14.4) trans :(7.6) cis :(8.5)
4	METHYLENECYCLOBUTENE (C_5H_6) (56.9)	trans : (24.8) cis : (25.7) (37.7) (37.2) trans : (26.2) cis : (27.1)

TABLE 5
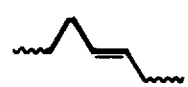
(contd.)

5	VINYLCYCLOPROPANE (C_5H_8) (28.8)	(10.5) (9.5) trans : (2.7) cis : (3.6)
6	CYCLOPENTENE (C_5H_8) 8.2	(−11.7) trans : (2.7) cis : (3.6)
7	1-1-DIMETHYLCYCLOPROPANE (C_5H_{10}) (2.0)	(−28.0)[b]
8	CYCLOHEXENE (C_6H_{10}) 1.1	(−23.3) trans : (−2.3) cis : (−1.4)

TABLE   5   (contd.)
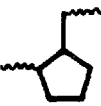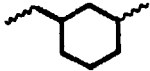
9	VINYLCYCLOBUTANE (C_6H_{10}) (25.5)	(4.6)	(-16.7)
10	1,5-HEXADIENE (C_6H_{10}) 20.0	(-16.7)	(-23.3)
11	NORBORNADIENE (C_7H_8) 55.7	(29.6)[c]	(26.7)[d]
12	NORBORNENE (C_7H_{10}) 20.9	(-6.4)	trans : (5.7) cis : (6.6)
13	1,6-HEPTADIENE (C_7H_{12}) (15.1)		(-28.2)

TABLE 5 (contd.)
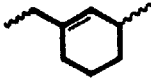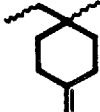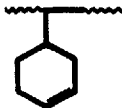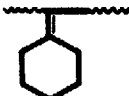
14	METHYLENECYCLOHEXENE (C_7H_{10}) (20.6)	 (-0.9)
15	2-METHYLENE-5-NORBORNENE (C_8H_{10}) (41.8)	 (23.8)[c]
16	1,4-DIMETHYLENECYCLOHEXANE (C_8H_{12}) (15.1)	 (-13.1)[e] (-7.7)
17	4-VINYLCYCLOHEXENE (C_8H_{12}) (11.3)	 (-3.2) (-8.6) (-11.3)[e]

TABLE   5   (contd.)
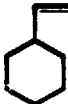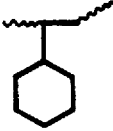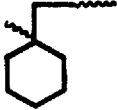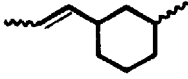
#	Compound	Structures
18	1,5-CYCLO-OCTADIENE (C_8H_{12}) (16.7)	cis : (−16.5)[f] trans:(−11.0)[f]
19	VINYLCYCLOHEXANE (C_8H_{14}) (−11.7)	(−32.4) (−34.9)
20	2,5-DIMETHYL-1,5-HEXADIENE (C_8H_{14}) (1.7)	(−27.8)[g]
21	2-VINYL-5-NORBORNENE (C_9H_{12}) (38.7)[d]	(11.5)[e] (11.5)[e] (−4.5)

TABLE   5   (contd.)
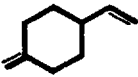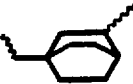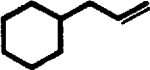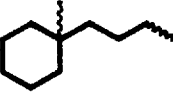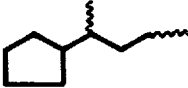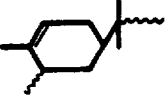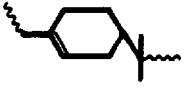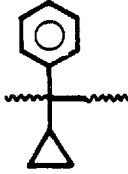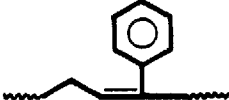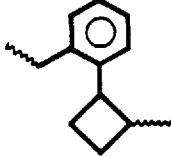
22	1-METHYLENE-4-VINYLCYCLO-HEXANE (C_9H_{14}) (17.9)	$(-21.9)^h$ (-10.1) $(-6.0)^g$
23	ALLYLCYCLOHEXANE (C_9H_{16}) (-16.3)	(-39.1) (-31.0)
24	α-PINENE ($C_{10}H_{16}$) 6.8	 (-23.7)
25	β-PINENE ($C_{10}H_{16}$) 9.3	 (-20.5)

TABLE   5   (contd.)

| 26 | STYRYLCYCLOPROPANE ($C_{11}H_{12}$)

 (50.3) | (34.6)

 (24.2)

 (33.9) |

aSystems mostly taken from Ref. 5. Values not parenthesized are experimental.

bDerived by using special bond energy terms for open chain alkanes polymers as in Part I [1].

cCalculated on the basis of a group contribution term for the nortricyclane (diradical) group, which is derived from the experimental $\Delta H_f°(g)$ for the molecule.

dOn the basis of a group contribution term for norbornene derived as above.

eOn the basis of a group contribution term derived from bicyclo-[2,2,1] heptane.

fOn the basis of a group contribution term derived from bicyclo-[3,3,0] octane

gTaking into account one [C₄C C₄]-interaction (= 5.26 kcal/mole, see Part II [1]) occurring outside the ring per repeat unit.

hOn the basis of a group contribution term derived from bicyclo-[2,2,2] octane.

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