

and added dropwise to a solution containing 10.8 mmol of diazomethane in 11 mL of ether at 0 °C, and the mixture was stirred for 30 min. The excess diazomethane was removed with argon, and the product was subjected to repetitive flash column chromatography (1:4 ethyl acetate-hexane) in order to separate the epimeric diazo ketones. In this manner 36 mg (14%) of the *Z* isomer **9q** and 77 mg (36%) of the *E* isomer (**9p**) were isolated. **9p**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 5.46 (s, 1 H), 3.11 (q, *J* = 7.5 Hz, 1 H), 1.85-1.24 (m, 10 H), 1.31 (s, 3 H) and 1.18 (d, *J* = 7.5 Hz, 3 H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 212.5, 192.8, 75.9, 61.2, 54.5, 42.0, 36.2, 28.1, 25.3, 24.0, 23.8, 15.7, 10.7; IR (CCl<sub>4</sub>) 3115, 2974, 2936, 2857, 2108, 1764, 1627, 1449, 1342, 1258, 1223, 1141, 1097, 1045, 1027, 964, 933, and 879 cm<sup>-1</sup>.

*Z* isomer, **9q**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 5.56 (m, 1 H), 3.16 (q, *J* = 7.3 Hz, 1 H), 1.84-1.18 (m, 10 H), 1.40 (s, 3 H), 1.17 (d, *J* = 7.3 Hz, 3 H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 213.0, 191.8, 72.7, 58.6, 54.4, 41.7, 34.4, 29.4, 25.4, 23.9, 23.4, 17.5, 10.0; IR (CCl<sub>4</sub>) 3115, 2937, 2856, 2109, 1762, 1624, 1454, 1368, 1345, 1260, 1244, 1226, 1149, 1118, 1037, 1009, 976, 914, 879, and 844 cm<sup>-1</sup>.

Pyrolysis of **9q**: Into a flask was placed 10 mL of xylene, and the solvent was heated to reflux before a solution of 30 mg of **9p** dissolved in 5 mL of xylene was added dropwise. After being heated for 30 min at reflux, the mixture was cooled and the solvent was evaporated to yield 23 mg of the spirocyclopropyl lactone **11p**. The stereochemistry was assigned on the basis of a 2% NOE observed for the cyclopropyl methyl group upon irradiation of the allylic methyl group of the Δ<sup>α,β</sup>-butenolide: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 5.80 (q, *J* = 1.5 Hz, 1 H), 2.13 (d, *J* = 1.5 Hz, 3 H), 1.86 (q, *J* = 6.9 Hz, 1 H), 1.62-1.23 (m, 10 H), 1.25 (d, *J* = 6.9 Hz, 3 H); <sup>13</sup>C NMR (63 MHz, DEPT, CDCl<sub>3</sub>) δ 172.9 (q), 168.0 (q), 117.5 (t), 77.7 (q), 39.0 (q), 34.4 (s), 26.2 (s), 26.0 (s), 25.6 (s), 25.4 (s), 33.3 (t), 17.0 (p), 8.5 (p); IR (CCl<sub>4</sub>) 2932, 2855, 1757, 1614, 1445, 1386, 1325, 1301, 1275, 1257, 1233, 1203, 1177, 1143, 1099, 1065, 1026, 1009, 994, 972, 937, 923, 861, and 842 cm<sup>-1</sup>; MS (70 eV) 206 (M<sup>+</sup>, 35), 191 (M<sup>+</sup> - Me, 5.6), 177 (M<sup>+</sup> - HCO, 7.7), 125 (100).

Pyrolysis of **9q**: The same procedure was employed as above using 35 mg (0.15 mmol) of the diazo ketone **9q**. After evaporation

of the solvent 31 mg (89%) of the lactone **11q** was isolated. TLC analysis showed that the reaction was stereospecific and none of the isomeric lactone **11p** was detected: **11q**: <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>) δ 5.76 (q, *J* = 1.4 Hz, 1 H), 2.01 (d, *J* = 1.4 Hz, 3 H), 1.96-1.17 (m, 11 H), 1.12 (d, *J* = 6.4 Hz, 3 H); <sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>) δ 173.3, 169.7, 115.5, 77.1, 37.8, 33.4, 31.0, 27.3, 26.1, 25.5, 25.2, 15.3 and 7.8; IR (CCl<sub>4</sub>) 2932, 2855, 1757, 1611, 1443, 1380, 1320, 1274, 1255, 1173, 1100, 967, 935, 919, and 842 cm<sup>-1</sup>; MS (70 eV) 206 (M<sup>+</sup>, 10), 191 (M<sup>+</sup> - HCO, 2.7), 125 (100). Consistent with the proposed stereochemical assignment, no NOE enhancement of the cyclopropyl methyl signal was observed upon irradiation of the allylic methyl group at δ 2.01. However, irradiation of this signal resulted on a 6% enhancement of the geometrically proximate vinyl hydrogen signal at δ 5.76.

**The Photochemical Generation and Thermal Rearrangement of α-Ketenylcyclobutanones.** Diazo ketones were dissolved in 20 mL of dry methylcyclohexane (*c* = (5-10) × 10<sup>-3</sup> M) placed in a Pyrex tube, sealed, and thoroughly degassed with argon. The tube was placed in a quartz dewar filled with methanol, surrounded by a circular filter tube of Corning 332 glass (transmission at 340 nm, 10%), and cooled to between -40 and -50 °C with a FTS systems immersion cooler. The apparatus was then placed in a Rayonet photochemical reactor (Southern New England Ultraviolet) fitted with 14 3500-Å lamps and irradiated until the diazo band (2110 cm<sup>-1</sup>) of the starting material was no longer detectable by IR (12-16 h). The tube was then removed and placed in a thermostated bath, and samples were withdrawn at intervals and analyzed by IR. The rate of disappearance of ketene was monitored by plotting ln(A - A<sub>0</sub>) for the ketene band at 2120 cm<sup>-1</sup> in the IR versus time. Solvent studies were conducted in a similar fashion. In this regard, the range of useful solvents is limited by the reactivity of the ketenes and their mode of generation.

**Supplementary Material Available:** Detailed X-ray spectral data (57 pages). Ordering information is given on any current masthead page.

## Experimental Formal Steric Enthalpy. 1. Alkanes and Cycloalkanes

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Received January 22, 1990

This study makes a critical evaluation of experimental values of formal steric enthalpies derived from published values of enthalpies of formation of alkanes and cycloalkanes (gas phase, 298 K). These provide primary data for calibration of force fields used in molecular mechanics.

This is the first of four papers describing studies of experimental formal steric enthalpies. These are derived from enthalpies of formation in the gas phase at 25 °C and are based on compilations by Cox and Pilcher<sup>1</sup> as revised by Pedley, Naylor, and Kirby<sup>2,3</sup> and from compilations of Stull, Westrum, and Sinke.<sup>4</sup> A few data are from other sources as listed.

Formal steric enthalpy (FSE) is a precisely defined measure of the steric component of the enthalpy of formation. It is the component that is to be computed by a

molecular mechanics calculation. The raw energy value computed in a molecular mechanics calculation may be designated as the steric energy (SE). SE values are of limited utility for estimating enthalpies of formation since they vary from one force field to another. Procedures are described elsewhere for a simple method to convert SE values derived from any force field to FSE values<sup>5,6</sup> providing that calibration of the force field is based on sound thermodynamic principles.

Equation 1 represents the empirical dissection of the enthalpy of formation of a compound in the gas phase into a bond component and a steric component. It is the basic variant of the traditional representations that are used to correlate thermochemical data.<sup>1,7</sup> Similar equations are successful with other thermochemical quantities, including

(1) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London and New York, 1970.

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(3) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: Cambridge, England, 1986.

(4) Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*; John Wiley & Sons, Inc.: New York, 1969.

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entropy and heat capacity; extensive tables of  $b$  increments, of steric corrections, and of increments for other thermochemical properties may be found in the work of Benson.<sup>7,8</sup> Equations 2 and 3 are variants suitable for use with molecular mechanics.

$$\Delta H_f = \sum n_i b_i + \text{steric term} \quad (1)$$

$$\Delta H_f - \text{SM} = \sum n_i c_i + \text{FSE} \quad (2)$$

$$\Delta H_f - \text{SM} = \sum n_i c_i + \text{SE} \quad (3)$$

According to eq 1 to 3, the contribution to the enthalpy of formation of a given structural element such as a methyl group or a methinyl group is independent of what else is present. This is true by definition. All deviations are attributed to "steric" terms.<sup>7,9</sup> The practical justification for adopting this definition is based on the fact that eq 1 gives an excellent correlation of enthalpies of formation with compounds for which the steric term is expected to be negligible or for those for which the steric term can be predicted adequately by a count of the number of gauche interactions and of correction terms for rings. See ref 10 for an example of extensive compilations of thermochemical data for substituted cyclopentanes and cyclohexanes based on this approach.

Pedley, Naylor, and Kirby<sup>3</sup> have proposed a more precise and more complex additivity procedure that incorporates some of the steric components in group increments. It is clear from the many examples in the literature that there is no one "best" method to carry out the dissection if the aim is empirical correlation of thermochemical data. The dissections in eqs 2 and 3 are the forms best suited for use with molecular mechanics estimates of steric terms.

The precision with which these empirical equations reproduce the experimental data may be seen from the summaries in Table IV below. For more than 100 alkanes and cycloalkanes the FSE value may be predicted within a standard deviation of 0.4 kcal/mol, the same as the estimated standard deviation of the enthalpies of formation data, by simply counting up gauche interactions and ring structures.

Thermodynamic properties pertain to populations of conformers. Butane, for example, has been reported to consist at room temperature of about 70% of the extended conformer and 30% of the two gauche conformers.<sup>11</sup> The experimental enthalpy of formation is about 0.27 kcal/mol more positive than the value that can be estimated for a hypothetical population consisting of 100% of the extended form.

The left-hand sides of eqs 2 and 3 define the enthalpy of formation of the single conformer of lowest energy; it is the experimental enthalpy of formation minus a value SM to correct for the contributions made by the other conformers to the experimental enthalpy of formation. Thus the  $b$  increments of eq 1 pertain to the ambient population of conformers while the  $c$  increments of eq 2 and the  $a$  increments of eq 3<sup>6,12</sup> pertain to the single conformer of lowest energy, the global minimum.

Equation 3 defines steric properties as the raw steric energy value that results from a molecular mechanics

calculation. The  $a$  increments are increments chosen so as to reproduce observed enthalpies of formation.<sup>13,14</sup> Any change of a force field that results in a change of the SE value calculated for a given conformer will require a recalculated set of  $a$  increments in order for eq 3 to be valid. Individual SE values such as in eq 3 have no fundamental significance. However, differences of SE values of isodesmic molecules are equal to differences of enthalpies of formation, and this relationship is of fundamental importance. (Isodesmic molecules have the same values of the  $\sum n_i a_i$  term in eq 3.)

Equation 2 is based on a different premise. The right-hand side expresses the left-hand side (the enthalpy of formation of the single conformer of lowest energy) as a bond term, the formal bond enthalpy FBE, described elsewhere as the "strain-free enthalpy of formation," plus a steric term, the formal steric enthalpy (FSE).<sup>5,12</sup> A common practice in estimating the "strain" of simple ring compounds is to use the steric term of eq 1 as the measure of "strain". In a similar sense the FSE value could, if desired, be used as an alternative definition of "strain". At one time it was common to see the SE values from a molecular mechanics calculation referred to as "strain", but this is definition of strain is no longer used much since the SE value of a given conformer differs from one force field to another.

However useful the concept of strain may be qualitatively, it is useful in computations only insofar as a precise definition is provided. It is important to note, for example, that "strain" as defined by eq 1 is different from "strain" (FSE) as defined by eq 2, and both are different from other proposed definitions of "strain".

According to eq 2 the FSE term bears the burden of all discrepancies between the sum of increments (the FBE term) and the "experimental" enthalpy of formation of the single conformer of lowest energy. The purpose of this study is to provide definitive experimental FSE values for most of the alkanes and cycloalkanes for which there are reported enthalpies of formation for the gas phase. It is the assumed task of a molecular mechanics calculation to reproduce the FSE values, that is, the part of the enthalpy of formation that is not accounted for by the sum of group increments that define the formal bond enthalpy.

**Estimation of SM Values.** The calculation of SM values is not a trivial problem. There are very few experimental values, butane and a few cyclohexanes are about all; see ref 15 for example.

One of the first to investigate the contributions of conformer populations to the enthalpy of formation and to define enthalpy values for individual alkane conformers was Mann, who specified "strain" in terms of gauche interactions.<sup>16,17</sup> This work was extended by Schleyer in a detailed analysis of strain in alkanes and cycloalkanes.<sup>12</sup> The representation in eq 2 is an extension of these earlier proposals.<sup>5,6,18</sup> Mann expressed steric effects as total gauche energies, that is as FSE plus SM in the present notation. A  $Z_g$  value of ref 17 when multiplied by the factor 0.70 is equal to SM plus the gauche component (FSE) for the molecule; the resulting SM values are comparable to those reported in this study.

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**Table I. Compounds Used To Derive  $c[\text{C-C-H-H-H}]$  and  $c[\text{C-C-C-H-H}]$  (All  $\Delta H_f$  Values Have Units of kcal/mol)<sup>a</sup>**

compound	formula	$\Delta H_f(\text{exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})^d$	FSE(exptl) <sup>e</sup>	FSE(assigned)
butane	C <sub>4</sub> H <sub>10</sub>	-30.15	S	-30.36	0.27	030.09	-0.06	0.00
butane	C <sub>4</sub> H <sub>10</sub>	-30.02	P	-30.36	0.27	-30.09	0.07	0.00
pentane	C <sub>5</sub> H <sub>12</sub>	-35.00	S	-35.51	0.47	-35.04	0.04	0.00
pentane	C <sub>5</sub> H <sub>12</sub>	-35.11	P	-35.51	0.47	-35.04	-0.07	0.00
hexane	C <sub>6</sub> H <sub>14</sub>	-39.94	P	-40.65	0.69	-39.96	0.02	0.00
hexane	C <sub>6</sub> H <sub>14</sub>	-39.96	S	-40.65	0.69	-39.96	0.00	0.00
heptane	C <sub>7</sub> H <sub>16</sub>	-44.86	P	-45.80	0.91	-44.89	0.03	0.00
heptane	C <sub>7</sub> H <sub>16</sub>	-44.88	S	-45.80	0.91	-44.89	0.01	0.00
octane	C <sub>8</sub> H <sub>18</sub>	-49.82	S	-50.95	1.12	-49.83	0.01	0.00
octane	C <sub>8</sub> H <sub>18</sub>	-49.86	P	-50.95	1.12	-49.83	-0.03	0.00

<sup>a</sup> Enthalpy of formation, kcal/mol, gas phase 25 °C. <sup>b</sup> P = Pedley, ref 3; S = Stull, ref 4. <sup>c</sup> FBE; sum of *c* increments calculated from these compounds. <sup>d</sup> FBE + SM. <sup>e</sup>  $H_f(\text{exptl})$  of column 3 -  $\Delta H_f(\text{calcd})$  of column 7. <sup>f</sup> These data lead to the following:  $c[\text{C-C-H-H-H}] = -10.333$ ;  $c[\text{C-C-C-H-H}] = -5.147$ .

**Table II. Compounds Used To Derive  $c[\text{C-C-C-C-H}]$  and  $c[\text{C-C-C-C-C}]$** 

compound	formula	$\Delta H_f(\text{Exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})^d$	FSE(exptl)	FSE(assigned)
2-methylbutane	C <sub>5</sub> H <sub>12</sub>	-36.74	P	-37.50	0.09	-37.41	0.67	0.70
2-methylbutane	C <sub>5</sub> H <sub>12</sub>	-36.92	S	-37.50	0.09	-37.41	0.49	0.70
2,2-dimethylbutane	C <sub>6</sub> H <sub>14</sub>	-44.35	S	-45.50	0.00	-45.50	1.15	1.40
2,2-dimethylbutane	C <sub>6</sub> H <sub>14</sub>	-44.48	P	-45.50	0.00	-45.50	1.02	1.40
2-methylpentane	C <sub>6</sub> H <sub>14</sub>	-41.66	S	-42.65	0.25	-42.40	0.74	0.70
2-methylpentane	C <sub>6</sub> H <sub>14</sub>	-41.78	P	-42.65	0.25	-42.40	0.62	0.70
2,2-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-49.27	S	-50.64	0.06	-50.58	1.31	1.40
2,2-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-49.21	P	-50.64	0.06	-50.58	1.37	1.40
2-methylhexane	C <sub>7</sub> H <sub>16</sub>	-46.51	P	-47.80	0.48	-47.32	0.81	0.70
2-methylhexane	C <sub>7</sub> H <sub>16</sub>	-46.59	S	-47.80	0.48	-47.32	0.73	0.70
2,2-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-53.68	P	-55.79	0.32	-55.47	1.79	1.40
2,2-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-53.71	S	-55.79	0.32	-55.47	1.76	1.40
2-methylheptane	C <sub>8</sub> H <sub>18</sub>	-51.48	P	-52.95	0.69	-52.26	0.78	0.70
2-methylheptane	C <sub>8</sub> H <sub>18</sub>	-51.50	S	-52.95	0.69	-52.26	0.76	0.70

<sup>a-c</sup> See Table I. <sup>f</sup> These data lead to the following:  $c[\text{C-C-C-C-H}] = -2.258$ ;  $c[\text{C-C-C-C-C}] = -0.217$ .

It is possible to get estimates of relative enthalpies of formation of conformers by molecular mechanics calculations. Because of uncertainties in the reliability of these values and of the difficulty of estimating entropy differences (probably relatively small), the only practical approach is to base calculations on enthalpies and on assumptions about conformer populations.

Various choices could be made for conformer energies. The gauche form of butane is reported to be 0.966 kcal/mol higher in energy than the extended form. The difference in energies of conformers of 2-methylbutane is reported to be 0.809 kcal/mol while the conformers of 2,3-dimethylbutane are of nearly equal energy.<sup>11</sup> Wiberg has investigated the relative energies of many conformers by ab initio methods;<sup>15</sup> the values range around 0.7 to 0.85.

The fraction of a given conformer present is found by calculating the Boltzmann distribution of conformers. The contribution to SM is the product of the fraction of a given conformer times its excess energy over the energy of the conformer that is the global minimum. Procedures have been described.<sup>19</sup> Fortunately the SM values are not very sensitive to the assumptions on which they are based. This is due to cancellations; the higher the energy assigned to a conformer, the less of it is present. As an example, the SM value for butane is calculated to be 0.23 for  $\Delta E = 0.5$  kcal/mol (for gauche - s-trans), 0.27 for 0.7, 0.27 for 0.9, 0.26 for 1.1, 0.21 for 1.5.

In order to treat large numbers of compounds, it is necessary to have fast automatic procedures. An approximate approach that is suitable for acyclic alkanes is to sum the energy of a conformer by counting all gauche interactions and adding suitable corrections for  $g^+g^-$  interactions. The summation is over all staggered conformers. There are nine conformers for a pentane, 27 for a

hexane, and so on. Although some conformers in large sets are impossible due to overlap, the multiple  $g^+g^-$  interactions present in such conformers guarantees that their presence or absence has negligible effect. The program STATAN was described some years ago, and this provided estimates for alkanes and methyl-branched alkanes.<sup>20</sup> In the present study I developed a new version using a more direct method of evaluating interactions of pairwise clusters. Results with the older program and the new one are identical except for a very few compounds having sequential CH(CH<sub>3</sub>) units, and the differences are small.

The SM calculations are based on assigned single gauche interactions of 0.70 kcal/mol and  $g^+g^-$  interactions totaling 3.3 kcal total. These are generally in accord with the values reported by Wiberg.<sup>15</sup> The SM values for butane and pentane are close to those obtained with various force fields. Using 0.80 for gauche interactions (instead of 0.70) increased SM values by less than 0.03 kcal/mol for any of the 18 polymethylpentanes. It is useful to note that as methylene groups are added to a chain, the first increment in SM is about 0.15 and subsequent increments are nearly constant at 0.215 kcal/mol.

Values were calculated for all of the methyl- and polymethyl-substituted pentanes and for many other alkanes with scattered methyl groups. Except for 2,3-dimethylbutane with an assigned SM of 0 (calculated 0.27), no attempt was made to allow for special gauche interactions for adjacent CH(CH<sub>3</sub>) units. Nor was it feasible to apply any special correction for multiple  $g^+$  interactions; Wiberg reports that the overall sum may be less than the sum of the separate interactions. Based on these tests, it appears that the errors in SM values are perhaps less than 10%. The largest value reported is 6.28 for dotriacontane, and errors in applying the 0.215 increment will be smoothly

Table III. Experimental Formal Steric Enthalpies of Alkanes and Cycloalkanes Based on Gas-Phase Enthalpies of Formation of 25 °C (All  $\Delta H_f$  Values Have Units of kcal/mol)

compound	formula	$\Delta H_f(\text{exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})$	FSE(exptl) <sup>e</sup>	FSE(ex-pected) <sup>f</sup>
ethane	C <sub>2</sub> H <sub>6</sub>	-20.08	S	-20.07	0.00	-20.07	-0.01	0.00
ethane	C <sub>2</sub> H <sub>6</sub>	-20.03	P	-20.07	0.00	-20.07	0.04	0.00
cyclopropane	C <sub>3</sub> H <sub>6</sub>	12.67	P	-15.44	0.00	-15.44	28.11	
cyclopropane	C <sub>3</sub> H <sub>6</sub>	12.74	S	-15.44	0.00	-15.44	28.18	
propane	C <sub>3</sub> H <sub>8</sub>	-24.82	S	-25.21	0.00	-25.21	0.39	0.00
propane	C <sub>3</sub> H <sub>8</sub>	-25.02	P	-25.21	0.00	-25.21	0.19	0.00
bicyclo[1.1.0]butane	C <sub>4</sub> H <sub>6</sub>	51.89	P	-14.81	0.00	-14.81	66.70	
cyclobutane	C <sub>4</sub> H <sub>8</sub>	6.37	S	-20.59	0.00	-20.59	26.96	
cyclobutane	C <sub>4</sub> H <sub>8</sub>	6.79	P	-20.59	0.00	-20.59	27.38	
2-methylpropane	C <sub>4</sub> H <sub>10</sub>	-32.07	P	-32.36	0.00	-32.36	0.29	0.00
2-methylpropane	C <sub>4</sub> H <sub>10</sub>	-32.15	S	-32.36	0.00	-32.36	0.21	0.00
spiropentane	C <sub>5</sub> H <sub>8</sub>	44.26	P	-20.81	0.00	-20.81	65.07	
1,1-dimethylcyclopropane	C <sub>5</sub> H <sub>10</sub>	-1.96	P	-30.58	0.00	-30.58	28.62	
cyclopentane	C <sub>5</sub> H <sub>10</sub>	-18.46	S	-25.74	0.00	-25.74	7.28	7.40 <sup>g</sup>
cyclopentane	C <sub>5</sub> H <sub>10</sub>	-18.26	P	-25.74	0.00	-25.74	7.48	7.40
2,2-dimethylpropane	C <sub>5</sub> H <sub>12</sub>	-39.67	S	-40.35	0.00	-40.35	0.68	0.00
2,2-dimethylpropane	C <sub>5</sub> H <sub>12</sub>	-40.18	P	-40.35	0.00	-40.35	0.17	0.00
bicyclo[3.1.0]hexane	C <sub>6</sub> H <sub>10</sub>	9.15	P	-25.10	0.00	-25.10	34.25	
bicyclopropyl	C <sub>6</sub> H <sub>10</sub>	30.93	P	-25.10	0.00	-25.10	56.03	
cyclohexane	C <sub>6</sub> H <sub>12</sub>	-29.43	S	-30.88	0.00	-30.88	1.45	1.40 <sup>b</sup>
cyclohexane	C <sub>6</sub> H <sub>12</sub>	-29.49	P	-30.88	0.00	-30.88	1.39	1.40
ethylcyclobutane	C <sub>6</sub> H <sub>12</sub>	-6.29	P	-32.88	0.00	-32.88	26.59	
methylcyclopentane	C <sub>6</sub> H <sub>12</sub>	-25.38	P	-32.88	0.00	-32.88	7.50	7.40
methylcyclopentane	C <sub>6</sub> H <sub>12</sub>	-25.50	S	-32.88	0.00	-32.88	7.38	7.40
2,3-dimethylbutane	C <sub>6</sub> H <sub>14</sub>	-42.49	S	-44.65	0.00	-44.65	2.16	
2,3-dimethylbutane	C <sub>6</sub> H <sub>14</sub>	-42.61	P	-44.65	0.00	-44.65	2.04	
3-methylpentane	C <sub>6</sub> H <sub>14</sub>	-41.02	S	-42.65	0.13	-42.52	1.50	1.40
3-methylpentane	C <sub>6</sub> H <sub>14</sub>	-41.13	P	-42.65	0.13	-42.52	1.39	1.40
quadricyclane	C <sub>7</sub> H <sub>8</sub>	81.05	P	-18.70	0.00	-18.70	99.75	
tricyclo[2.2.1.0 <sup>2,6</sup> ]heptane	C <sub>7</sub> H <sub>10</sub>	19.62	P	-24.47	0.00	-24.47	44.09	
tricyclo[4.1.0.0 <sup>2,4</sup> ]heptane	C <sub>7</sub> H <sub>10</sub>	35.66	P	-24.47	0.00	-24.47	60.13	
1-methylbicyclo[3.1.0]hexane	C <sub>7</sub> H <sub>12</sub>	0.36	P	-33.10	0.00	-33.10	33.46	
bicyclo[2.2.1]heptane	C <sub>7</sub> H <sub>12</sub>	-13.12	P	-30.25	0.00	-30.25	17.13	
bicyclo[4.1.0]heptane	C <sub>7</sub> H <sub>12</sub>	0.36	P	-30.25	0.00	-30.25	30.61	
1,1-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-33.03	P	-40.87	0.00	-40.87	7.84	
1,1-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-33.05	S	-40.87	0.00	-40.87	7.82	
<i>trans</i> -1,2-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-32.67	S	-40.02	0.00	-40.02	7.35	
<i>cis</i> -1,2-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-30.95	P	-40.02	0.00	-40.02	9.07	
<i>cis</i> -1,2-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-30.96	S	-40.02	0.00	-40.02	9.06	
<i>trans</i> -1,2-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-32.65	P	-40.02	0.00	-40.02	7.37	
<i>cis</i> -1,3-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-32.47	S	-40.02	0.00	-40.02	7.55	7.40
<i>cis</i> -1,3-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-32.48	P	-40.02	0.00	-40.02	7.54	7.40
<i>trans</i> -1,3-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-31.93	P	-40.02	0.00	-40.02	8.09	
<i>trans</i> -1,3-dimethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-31.93	S	-40.02	0.00	-40.02	8.09	
cycloheptane	C <sub>7</sub> H <sub>14</sub>	-28.23	P	-36.03	0.07	-35.96	7.73	
cycloheptane	C <sub>7</sub> H <sub>14</sub>	-28.52	S	-36.03	0.07	-35.96	7.44	
ethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-30.33	P	-38.03	0.09	-37.94	7.61	7.40
ethylcyclopentane	C <sub>7</sub> H <sub>14</sub>	-30.37	S	-38.03	0.09	-37.94	7.57	7.40
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	-36.97	P	-38.03	0.07	-37.96	0.99	1.40
methylcyclohexane	C <sub>7</sub> H <sub>14</sub>	-36.99	S	-38.03	0.07	-37.96	0.97	1.40
2,2,3-trimethylbutane	C <sub>7</sub> H <sub>16</sub>	-48.88	P	-52.64	0.00	-52.64	3.76	
2,2,3-trimethylbutane	C <sub>7</sub> H <sub>16</sub>	-48.95	S	-52.64	0.00	-52.64	3.69	
2,3-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-47.54	P	-49.80	0.24	-49.56	2.02	
2,3-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-47.62	S	-49.80	0.24	-49.56	1.94	
2,4-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-48.21	P	-49.80	0.13	-49.67	1.46	
2,4-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-48.28	S	-49.80	0.13	-49.67	1.39	
3,3-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-48.09	P	-50.64	0.02	-50.62	2.53	2.80
3,3-dimethylpentane	C <sub>7</sub> H <sub>16</sub>	-48.17	S	-50.64	0.02	-50.62	2.45	2.80
3-ethylpentane	C <sub>7</sub> H <sub>16</sub>	-45.32	P	-47.80	0.51	-47.29	1.97	
3-ethylpentane	C <sub>7</sub> H <sub>16</sub>	-45.33	S	-47.80	0.51	-47.29	1.96	
3-methylhexane	C <sub>7</sub> H <sub>16</sub>	-45.72	P	-47.80	0.30	-47.50	1.78	1.40
3-methylhexane	C <sub>7</sub> H <sub>16</sub>	-45.96	S	-47.80	0.30	-47.50	1.54	1.40
cubane	C <sub>8</sub> H <sub>8</sub>	148.69	P	-18.06	0.00	-18.06	166.75	
1-methylbicyclo[4.1.0]heptane	C <sub>8</sub> H <sub>14</sub>	-4.97	P	-38.24	0.00	-38.24	33.27	
bicyclo[2.2.2]octane	C <sub>8</sub> H <sub>14</sub>	-23.66	P	-35.40	0.00	-35.40	11.74	
<i>cis</i> -Bicyclo[3.3.0]octane	C <sub>8</sub> H <sub>14</sub>	-22.20	P	-35.40	0.00	-35.40	13.20	
<i>trans</i> -bicyclo[3.3.0]octane	C <sub>8</sub> H <sub>14</sub>	-15.92	P	-35.40	0.00	-35.40	19.48	
cyclo[4.2.0]octane	C <sub>8</sub> H <sub>14</sub>	-6.26	P	-35.40	0.00	-35.40	29.14	
bicyclo[5.1.0]octane	C <sub>8</sub> H <sub>14</sub>	-3.97	P	-35.40	0.00	-35.40	31.43	
1,1-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-43.24	P	-46.02	0.00	-46.02	2.78	
1,1-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-43.26	S	-46.02	0.00	-46.02	2.76	
<i>cis</i> -1,2-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-41.15	S	-45.17	0.00	-45.17	4.02	
<i>cis</i> -1,2-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-41.13	P	-45.17	0.00	-45.17	4.04	
<i>trans</i> -1,2-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-43.00	P	-45.17	0.00	-45.17	2.17	2.10 <sup>g</sup>
<i>trans</i> -1,2-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-43.02	S	-45.17	0.00	-45.17	2.15	2.10
<i>cis</i> -1,3-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-44.12	P	-45.17	0.00	-45.17	1.05	1.40

Table III (Continued)

compound	formula	$\Delta H_f(\text{exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})$	FSE(exptl) <sup>e</sup>	FSE(ex- pected) <sup>f</sup>
<i>cis</i> -1,3-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-44.16	S	-45.17	0.00	-45.17	1.01	1.40
<i>trans</i> -1,3-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-42.18	P	-45.17	0.00	-45.17	2.99	
<i>trans</i> -1,3-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-42.20	S	-45.17	0.00	-45.17	2.97	
<i>cis</i> -1,4-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-42.21	P	-45.17	0.00	-45.17	2.96	
<i>cis</i> -1,4-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-42.22	S	-45.17	0.00	-45.17	2.95	
<i>trans</i> -1,4-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-44.10	P	-45.17	0.00	-45.17	1.07	1.40
<i>trans</i> -1,4-dimethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-44.12	S	-45.17	0.00	-45.17	1.05	1.40
cyclooctane	C <sub>8</sub> H <sub>16</sub>	-29.73	P	-41.18	0.15	-41.03	11.30	
cyclooctane	C <sub>8</sub> H <sub>16</sub>	-30.06	S	-41.18	0.15	-41.03	10.97	
ethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-41.05	S	-43.17	0.09	-43.08	2.03	1.40
ethylcyclohexane	C <sub>8</sub> H <sub>16</sub>	-41.04	P	-43.17	0.09	-43.08	2.04	1.40
propylcyclopentane	C <sub>8</sub> H <sub>16</sub>	-35.30	P	-43.17	0.25	-42.92	7.62	7.40
propylcyclopentane	C <sub>8</sub> H <sub>16</sub>	-35.39	S	43.17	0.25	-42.92	7.53	7.40
2,2,3,3-tetramethylbutane	C <sub>8</sub> H <sub>18</sub>	-53.92	P	-60.63	0.00	-60.63	6.71	
2,2,3,3-tetramethylbutane	C <sub>8</sub> H <sub>18</sub>	-53.99	S	-60.63	0.00	-60.63	6.64	
2,2,3-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-52.58	P	-57.79	0.10	-57.69	5.11	
2,2,3-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-52.61	S	-57.79	0.10	-57.69	5.08	
2,2,4-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-53.54	P	-57.79	0.02	-57.77	4.23	
2,2,4-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-53.57	S	-57.79	0.02	-57.77	4.20	
2,3,3-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-51.70	P	-57.79	0.10	-57.69	5.99	
2,3,3-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-51.73	S	-57.79	0.10	-57.69	5.96	
2,3,4-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-51.94	P	-56.94	0.25	-56.69	4.75	
2,3,4-trimethylpentane	C <sub>8</sub> H <sub>18</sub>	-51.97	S	-56.94	0.25	-56.69	4.72	
2,3-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-51.10	P	-54.94	0.64	-54.30	3.20	
2,3-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-51.13	S	-54.94	0.64	-54.30	3.17	
2,4-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-52.39	P	-54.94	0.18	-54.76	2.37	
2,4-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-52.44	S	-54.94	0.18	-54.76	2.32	
2,5-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-53.18	P	-54.94	0.27	-54.67	1.49	1.40
2,5-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-53.21	S	-54.94	0.27	-54.67	1.46	1.40
3,3-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-52.58	P	-55.79	0.08	-55.71	3.13	2.80
3,3-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-52.61	S	-55.79	0.08	-55.71	3.10	2.80
3,4-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-50.86	P	-54.94	0.21	-54.73	3.87	
3,4-dimethylhexane	C <sub>8</sub> H <sub>18</sub>	-50.91	S	-54.94	0.21	-54.73	3.82	
3-ethyl-2-methylpentane	C <sub>8</sub> H <sub>18</sub>	-50.43	P	-54.94				
3-ethyl-2-methylpentane	C <sub>8</sub> H <sub>18</sub>	-50.48	S	-54.94				
3-ethyl-3-methylpentane	C <sub>8</sub> H <sub>18</sub>	-51.34	P	-55.79				
3-ethyl-3-methylpentane	C <sub>8</sub> H <sub>18</sub>	-51.38	S	-55.79				
3-ethylhexane	C <sub>8</sub> H <sub>18</sub>	-50.36	P	-52.95	0.73	-52.22	1.86	
3-ethylhexane	C <sub>8</sub> H <sub>18</sub>	-50.40	S	-52.95	0.73	-52.22	1.82	
3-methylheptane	C <sub>8</sub> H <sub>18</sub>	-50.79	P	-52.95	0.52	-52.43	1.64	1.40
3-methylheptane	C <sub>8</sub> H <sub>18</sub>	-50.82	S	-52.95	0.52	-52.43	1.61	1.40
4-methylheptane	C <sub>8</sub> H <sub>18</sub>	-50.67	P	-52.95	0.69	-52.26	1.59	1.40
4-methylheptane	C <sub>8</sub> H <sub>18</sub>	-50.69	S	-52.95	0.69	-52.26	1.57	1.40
1,4-dimethylbicyclo[2.2.1]heptane	C <sub>9</sub> H <sub>16</sub>	-30.62	P	-46.24	0.00	-46.24	15.62	
<i>trans</i> -2,3-dimethylbicyclo[2.2.1]heptane	C <sub>9</sub> H <sub>16</sub>	-25.69	P	-46.24	0.00	-46.24	20.55	
bicyclo[3.3.1]nonane	C <sub>9</sub> H <sub>16</sub>	-30.47	P	-40.55	0.00	-40.55	10.08	
<i>cis</i> -bicyclo[4.3.0]nonane	C <sub>9</sub> H <sub>16</sub>	-30.38	P	-40.55	0.00	-40.55	10.17	
<i>trans</i> -bicyclo[4.3.0]nonane	C <sub>9</sub> H <sub>16</sub>	-31.43	P	-40.55	0.00	-40.55	9.12	
<i>trans</i> -(+)-bicyclo[6.1.0]nonane	C <sub>9</sub> H <sub>16</sub>	-9.49	P	-40.55	0.00	-40.55	31.06	
<i>cis</i> -bicyclo[6.1.0]nonane	C <sub>9</sub> H <sub>16</sub>	-7.43	P	-40.55	0.00	-40.55	33.12	
<i>cis,cis</i> -1,3,5-trimethylcyclohexane	C <sub>9</sub> H <sub>18</sub>	-50.69	P	-52.31	0.00	-52.31	1.62	1.40
<i>cis,cis</i> -1,3,5-trimethylcyclohexane	C <sub>9</sub> H <sub>18</sub>	-51.48	S	-52.31	0.00	-52.31	0.83	1.40
<i>cis,trans</i> -1,3,5-trimethylcyclohexane	C <sub>9</sub> H <sub>18</sub>	-49.37	S	-52.31	0.07	-52.24	2.87	
butylcyclopentane	C <sub>9</sub> H <sub>18</sub>	-40.22	S	-48.32	0.48	-47.84	7.62	7.40
cyclononane	C <sub>9</sub> H <sub>18</sub>	-31.74	P	-46.32				
propylcyclohexane	C <sub>9</sub> H <sub>18</sub>	-46.01	P	-48.32	0.25	-48.07	2.06	1.40
propylcyclohexane	C <sub>9</sub> H <sub>18</sub>	-46.20	S	-48.32	0.25	-48.07	1.87	1.40
2,2,3,3-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.67	P	-65.78	0.14	-65.64	8.97	
2,2,3,3-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.70	S	-65.78	0.14	-65.64	8.94	
2,2,3,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.62	P	-64.93	0.19	-64.74	8.12	
2,2,3,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.64	S	-64.93	0.19	-64.74	8.10	
2,2,3-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-57.65	S	-62.93	0.28	-62.65	5.00	
2,2,4,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-57.74	P	-65.78	0.00	-65.78	8.04	
2,2,4,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-57.83	S	-65.78	0.00	-65.78	7.95	
2,2,4-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-58.13	S	-62.93	0.07	-62.86	4.73	
2,2,5-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-60.71	S	-62.93	0.07	-62.86	2.15	
2,2-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-59.00	S	-60.94	0.53	-60.41	1.41	1.40
2,3,3,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.43	P	-64.93	0.21	-64.72	8.29	
2,3,3,4-tetramethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.46	S	-64.93	0.21	-64.72	8.26	
2,3,3-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-57.08	S	-62.93	0.12	-62.81	5.73	
2,3,4-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-56.18	S	-62.09	0.22	-61.87	5.69	
2,3,5-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-58.03	S	-62.09	0.30	-61.79	3.76	
2,3-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-56.32	S	-60.09	0.64	-59.45	3.13	
2,4,4-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-57.56	S	-62.93	0.04	-62.89	5.33	
2,4-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-57.48	S	-60.09	0.35	-59.74	2.26	
2,5-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-57.48	S	-60.09	-0.31	-59.78	2.30	2.10
2,6-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-58.17	S	-60.09	0.47	-59.62	1.45	1.40

Table III (Continued)

compound	formula	$\Delta H_f(\text{exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})$	FSE(exptl) <sup>e</sup>	FSE(ex- pected) <sup>f</sup>
2-methyloctane	C <sub>9</sub> H <sub>20</sub>	-56.45	S	-58.09	0.91	-57.18	0.73	0.70
3,3,4-trimethylhexane	C <sub>9</sub> H <sub>20</sub>	-56.39	S	-62.93	0.16	-62.77	6.38	
3,3-diethylpentane	C <sub>9</sub> H <sub>20</sub>	-55.52	P	-60.94				
3,3-diethylpentane	C <sub>9</sub> H <sub>20</sub>	-55.44	S	-60.94				
3,3-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-57.74	S	-60.94	0.34	-60.60	2.86	2.80
3,4-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-55.63	S	-60.09	0.39	-59.70	4.07	
3,5-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-56.79	S	-60.09	0.23	-59.86	3.07	
3-ethyl-2,2-dimethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.96	S	-62.93				
3-ethyl-2,3-dimethylpentane	C <sub>9</sub> H <sub>20</sub>	-55.82	S	-62.93				
3-ethyl-2,4-dimethylpentane	C <sub>9</sub> H <sub>20</sub>	-56.18	S	-62.93				
3-ethyl-2-methylhexane	C <sub>9</sub> H <sub>20</sub>	-55.63	S	-60.09				
3-ethyl-3-methylhexane	C <sub>9</sub> H <sub>20</sub>	-56.48	S	-60.94				
3-ethyl-4-methylhexane	C <sub>9</sub> H <sub>20</sub>	-54.94	S	-60.09				
3-ethylheptane	C <sub>9</sub> H <sub>20</sub>	-55.08	S	-58.09	0.92	-57.17	2.09	
3-methyloctane	C <sub>9</sub> H <sub>20</sub>	-55.77	S	-58.09	0.74	-57.35	1.58	1.40
4,4-dimethylheptane	C <sub>9</sub> H <sub>20</sub>	-57.74	S	-60.94	0.15	-60.79	3.05	2.80
4-ethyl-2-methylhexane	C <sub>9</sub> H <sub>20</sub>	-56.79	S	-60.09				
4-ethylheptane	C <sub>9</sub> H <sub>20</sub>	-55.08	S	-58.09	0.80	-57.29	2.21	
4-methyloctane	C <sub>9</sub> H <sub>20</sub>	-55.77	S	-58.09	0.69	-57.40	1.63	1.40
nonane	C <sub>9</sub> H <sub>20</sub>	-54.54	P	-56.10	1.33	-54.77	0.23	0.00
nonane	C <sub>9</sub> H <sub>20</sub>	-54.74	S	-56.10	1.33	-54.77	0.03	0.00
adamantane	C <sub>10</sub> H <sub>16</sub>	-32.17	P	-39.91	0.00	-39.91	7.74	
octahydro-4,7-methanoindan	C <sub>10</sub> H <sub>16</sub>	-14.34	P	-39.91	0.00	-39.91	25.57	
protoadamantane	C <sub>10</sub> H <sub>16</sub>	-20.53	P	-39.91	0.00	-39.91	19.38	
bicyclo[3.3.2]decane	C <sub>10</sub> H <sub>18</sub>	-25.36	P	-45.69	0.00	-45.69	20.33	
cis-bicyclo[4.4.0]decane (decalin)	C <sub>10</sub> H <sub>18</sub>	-40.44	P	-45.69	0.00	-45.69	5.25	
trans-bicyclo[4.4.0]decane (decalin)	C <sub>10</sub> H <sub>18</sub>	-43.52	P	-45.69	0.00	-45.69	2.17	2.60 <sup>j</sup>
bicyclo[5.3.0]decane	C <sub>10</sub> H <sub>18</sub>	-31.26	P	-45.69	0.00	-45.69	14.43	
spiro[4.5]decane	C <sub>10</sub> H <sub>18</sub>	-34.68	P	-46.54	0.00	-46.54	11.86	
trans-3,7,7-trimethylbicyclo[4.1.0]heptane	C <sub>10</sub> H <sub>18</sub>	-17.23	P	-52.53	0.00	-52.53	35.30	
cis-3,7,7-trimethylbicyclo[4.1.0]heptane	C <sub>10</sub> H <sub>18</sub>	-16.68	P	-52.53	0.00	-52.53	35.85	
1-methyl-4-isopropylcyclohexane	C <sub>10</sub> H <sub>20</sub>	-55.14	P	-57.46	0.00	-57.46	2.32	
butylcyclohexane	C <sub>10</sub> H <sub>20</sub>	-50.98	P	-53.47	0.48	-52.99	2.01	1.40
butylcyclohexane	C <sub>10</sub> H <sub>20</sub>	-50.95	S	-53.47	0.48	-52.99	2.04	1.40
cyclodecane	C <sub>10</sub> H <sub>20</sub>	-36.88	P	-51.47				
pentylcyclopentane	C <sub>10</sub> H <sub>20</sub>	-45.15	S	-53.47	0.69	-52.78	7.63	7.40
2-methylnonane	C <sub>10</sub> H <sub>22</sub>	-61.38	S	-63.24	1.12	-62.12	0.74	0.70
2-methylnonane	C <sub>10</sub> H <sub>22</sub>	-62.12	P	-63.24	1.12	-62.12	0.00	0.70
3-methylnonane	C <sub>10</sub> H <sub>22</sub>	-60.70	S	-63.24	0.95	-62.29	1.59	1.40
4-methylnonane	C <sub>10</sub> H <sub>22</sub>	-60.70	S	-63.24	0.90	-62.34	1.64	1.40
5-methylnonane	C <sub>10</sub> H <sub>22</sub>	-60.70	S	-63.24	0.91	-62.33	1.63	1.40
5-methylnonane	C <sub>10</sub> H <sub>22</sub>	-61.81	P	-63.24	0.91	-62.33	0.52	1.40
decane	C <sub>10</sub> H <sub>22</sub>	-59.63	P	-61.24	1.55	-59.69	0.06	0.00
decane	C <sub>10</sub> H <sub>22</sub>	-59.67	S	-61.24	1.55	-59.69	0.02	0.00
1-methyladamantane	C <sub>11</sub> H <sub>18</sub>	-41.01	P	-47.91	0.00	-47.91	6.90	
2-methyladamantane	C <sub>11</sub> H <sub>18</sub>	-36.26	P	-47.91	0.00	-47.91	11.65	
bicyclo[3.3.3]undecane	C <sub>11</sub> H <sub>20</sub>	-21.27	P	-50.84	0.00	-50.84	29.57	
spiro[5.5]undecane	C <sub>11</sub> H <sub>20</sub>	-45.00	P	-51.69	0.00	-51.69	6.69	
cycloundecane	C <sub>11</sub> H <sub>22</sub>	-42.88	P	-56.62				
hexylcyclopentane	C <sub>11</sub> H <sub>22</sub>	-50.07	S	-58.61	0.91	-57.70	7.63	7.40
pentylcyclohexane	C <sub>11</sub> H <sub>22</sub>	-55.88	S	-58.61	0.69	-57.92	2.04	
2,2,4,4,5-pentamethylhexane	C <sub>11</sub> H <sub>24</sub>	-67.16	P	-78.07	0.06	-78.01	10.85	
2,2,5,5-tetramethylheptane	C <sub>11</sub> H <sub>24</sub>	-72.28	P	-76.07	0.03	-76.04	3.76	
3,3,5,5-tetramethylheptane	C <sub>11</sub> H <sub>24</sub>	-66.13	P	-76.07	0.04	-76.03	9.90	
undecane	C <sub>11</sub> H <sub>24</sub>	-64.60	S	-66.39	1.76	-64.63	0.03	0.00
undecane	C <sub>11</sub> H <sub>24</sub>	-64.75	P	-66.39	1.76	-64.63	-0.12	0.00
1,3-dimethyladamantane	C <sub>12</sub> H <sub>20</sub>	-43.67	P	-55.90	0.00	-55.90	12.23	
2,2-dimethyladamantane	C <sub>12</sub> H <sub>20</sub>	-43.67	P	-55.05	0.00	-55.05	11.38	
cyclododecane	C <sub>12</sub> H <sub>24</sub>	-55.02	P	-61.76				
bicyclohexyl	C <sub>12</sub> H <sub>22</sub>	-51.55	P	-55.99	0.00	-55.99	4.44	2.80
heptylcyclopentane	C <sub>12</sub> H <sub>24</sub>	-55.00	S	-63.76	1.12	-62.64	7.64	7.40
hexylcyclohexane	C <sub>12</sub> H <sub>24</sub>	-60.80	S	-63.76	0.91	-62.85	2.05	
3,3,6,6-tetramethyloctane	C <sub>12</sub> H <sub>26</sub>	-76.05	P	-81.22	0.05	-81.17	5.12	
dodecane	C <sub>12</sub> H <sub>26</sub>	-69.24	P	-71.54	1.98	-69.56	0.32	0.00
dodecane	C <sub>12</sub> H <sub>26</sub>	-69.52	S	-71.54	1.98	-69.56	0.04	0.00
1,3,5-trimethyladamantane	C <sub>13</sub> H <sub>22</sub>	-60.83	P	-63.89	0.00	-63.89	3.06	
cyclotridecane	C <sub>13</sub> H <sub>26</sub>	-58.89	P	-66.91				
heptylcyclohexane	C <sub>13</sub> H <sub>26</sub>	-69.12	P	-68.91	1.12	-67.79	-1.33	1.40
heptylcyclohexane	C <sub>13</sub> H <sub>26</sub>	-65.73	S	-68.91	1.12	-67.79	2.06	1.40
octylcyclopentane	C <sub>13</sub> H <sub>26</sub>	-59.92	S	-68.91	1.34	-67.57	7.65	7.40
3,5-diethyl-3,5-dimethylheptane	C <sub>13</sub> H <sub>28</sub>	-72.01	P	-86.37				
4,4,6,6-tetramethylnonane	C <sub>13</sub> H <sub>28</sub>	-74.86	P	-86.37	0.17	-86.20	11.34	
tri-tert-butylmethane	C <sub>13</sub> H <sub>28</sub>	-56.40	O*	-93.21	0.00	-93.21	36.81	
tridecane	C <sub>13</sub> H <sub>28</sub>	-74.45	S	-76.68	2.20	-74.48	0.03	0.00
diamantane	C <sub>14</sub> H <sub>20</sub>	-34.87	P	-48.95	0.00	-48.95	14.08	
1,3,5,7-tetramethyladamantane	C <sub>14</sub> H <sub>24</sub>	-67.73	P	-71.88	0.00	-71.88	4.15	

Table III (Continued)

compound	formula	$\Delta H_f(\text{exptl})^a$	ref <sup>b</sup>	FBE <sup>c</sup>	SM	$\Delta H_f(\text{calcd})$	FSE(exptl) <sup>e</sup>	FSE(ex-pected) <sup>f</sup>
<i>trans,anti,trans</i> -tetradecahydroanthracene	C <sub>14</sub> H <sub>24</sub>	-52.72	P	-60.50	0.00	-60.50	7.78	
<i>trans,syn,trans</i> -tetradecahydroanthracene	C <sub>14</sub> H <sub>24</sub>	-58.13	P	-60.50	0.00	-60.50	2.37	3.70 <sup>l</sup>
cyclotetradecane	C <sub>14</sub> H <sub>28</sub>	-57.17	P	-72.06				
octylcyclohexane	C <sub>14</sub> H <sub>28</sub>	-70.65	S	-74.06	1.34	-72.72	2.07	1.40
tetradecane	C <sub>14</sub> H <sub>30</sub>	-79.38	S	-81.83	2.41	-79.42	0.04	0.00
1-methyldiamantane	C <sub>15</sub> H <sub>22</sub>	-39.84	P	-56.94	0.00	-56.94	17.10	
3-methyldiamantane	C <sub>15</sub> H <sub>22</sub>	-37.60	P	-56.94	0.00	-56.94	19.34	
4-methyldiamantane	C <sub>15</sub> H <sub>22</sub>	-42.52	P	-56.94	0.00	-56.94	13.42	
cyclopentadecane	C <sub>15</sub> H <sub>30</sub>	-72.04	P	-77.21				
nonylcyclohexane	C <sub>15</sub> H <sub>30</sub>	-75.58	S	-79.20	1.56	-77.64	2.06	1.40
4,6-diethyl-4,6-dimethylnonane	C <sub>15</sub> H <sub>32</sub>	-82.96	P	-96.66				
5,5,7,7-tetramethylundecane	C <sub>15</sub> H <sub>32</sub>	-87.62	P	-96.66	0.42	-96.24	8.62	
pentadecane	C <sub>15</sub> H <sub>32</sub>	-84.31	S	-86.98	2.63	-84.35	0.04	0.00
decylcyclohexane	C <sub>16</sub> H <sub>32</sub>	-81.14	P	-84.35	1.77	-82.58	1.44	1.40
cyclohexadecane	C <sub>16</sub> H <sub>32</sub>	-76.89	P	-82.35				
hexadecane	C <sub>16</sub> H <sub>34</sub>	-89.23	S	-92.12	2.84	-89.28	0.05	0.00
hexadecane	C <sub>16</sub> H <sub>34</sub>	-89.58	P	-92.12	2.84	-89.28	-0.30	0.00
cycloheptadecane	C <sub>17</sub> H <sub>34</sub>	-87.07	P	-87.50				
dodecylcyclohexane	C <sub>18</sub> H <sub>36</sub>	-90.51	P	-94.64	2.20	-92.44	1.93	1.40
octadecane	C <sub>18</sub> H <sub>38</sub>	-99.08	S	-102.42	3.27	-99.15	0.07	0.00
octadecane	C <sub>18</sub> H <sub>38</sub>	-99.14	P	-102.42	3.27	-99.15	0.01	0.00
<i>sym</i> -tetra- <i>tert</i> -butylethane	C <sub>18</sub> H <sub>38</sub>	-59.90	O <sup>m</sup>	-125.78	0.00	-125.78	65.88	
hexadecylcyclopentane	C <sub>21</sub> H <sub>42</sub>	-99.33	S	-110.08	3.06	-107.02	7.69	7.40
11-butyldocosane	C <sub>26</sub> H <sub>54</sub>	-141.83	P	-145.59				
5-butyldocosane	C <sub>26</sub> H <sub>54</sub>	-140.44	P	-145.59				
11-decylheneicosane	C <sub>31</sub> H <sub>64</sub>	-168.69	P	-171.33				
dotriacontane	C <sub>32</sub> H <sub>66</sub>	-166.63	P	-174.48	6.28	-168.20	1.57	0.00

<sup>a</sup> kcal/mol, gas phase 25 °C. <sup>b</sup> A, average value; O, reference as marked; P, Pedley Naylor, and Kirby;<sup>2,3</sup> S, Stull et al.<sup>4</sup> <sup>c</sup> Based on increments of Tables I and II. <sup>d</sup> Value of column 5 plus value of column 6. <sup>e</sup> Value of column 3 minus value of column 7. <sup>f</sup> See text; 0.70 per gauche interaction. <sup>g</sup> FSE value for cyclopentane is average of the compounds having a 7.40 entry. <sup>h</sup> FSE value for cyclohexane is average of compounds having a 1.40 entry. <sup>i</sup> *trans*-1,2-Dimethylcyclohexane has one gauche interaction plus the cyclohexane ring. <sup>j</sup> Decalin FSE is estimated as having 11 cyclohexane type torsions; 14\*(1.4/6). <sup>k</sup> Reference 23. <sup>l</sup> Perhydroanthracene estimated as 16\*(1.4/6). <sup>m</sup> Reference 24.

progressive. The question as to whether these estimates of errors are overly optimistic must be left for the future.

For rings up through cyclohexane SM is 0. For cycloheptane and cyclooctane SM is less than 0.1 kcal/mol on the basis of the reported conformer calculations.<sup>13,21</sup> This assumes that we can treat the "pseudorotation" families as units, ignoring possible entropic effects. Calculations were not made for ethyl-substituted alkanes, nor were estimates made for larger rings, and therefore SM values are not available for these. For compounds made up of six-membered or smaller rings, SM is 0 if unsubstituted or methyl-substituted; if longer alkyl side chains are present, the ring was treated as though it is an isopropyl group.

**Enthalpies of Formation.** Equations 1 to 3 may be used in three different ways. Equation 2, for example, can be used to calculate *c* increments. These are derived from sets of molecules of defined FSE values along with their enthalpies of formation and appropriate SM values.<sup>6,12</sup> This approach is illustrated in Tables I and II. Equation 2 can then be used to calculate experimental FSE values of other compounds, given the *c* increments, the enthalpies of formation, and SM values. Equation 2 can also be used to calculate enthalpies of formation, given the *c* increments, estimated SM values, and the FSE values obtained by applying suitable corrections to SE values obtained from a molecular mechanics calculation.<sup>5,6,9,18,22</sup>

In order to calculate the *c* increments, it is necessary to define the FSE values of the lowest energy conformers of standard molecules. A customary choice is to treat the

extended conformers of *n*-alkanes as strain free; they are defined to have FSE = 0. With appropriate estimates of SM values and with enthalpies of formation of *n*-alkanes, equation 2 is used to calculate *c*[C\_C\_H\_H\_H\_] and *c*[C\_C\_C\_H\_H\_]; these are *c* increments for a methyl group attached to an sp<sup>3</sup> carbon atom and for a methylene group attached to two sp<sup>3</sup> carbon atoms. The formal steric enthalpy of isoalkanes can be assigned the value 0.70, and FSE for neoalkanes the value 1.40. These FSE assignments permit the calculation of *c*[C\_C\_C\_C\_H\_] and of *c*[C\_C\_C\_C\_C\_]. The choices of standards are of necessity arbitrary ones; these particular standards for FSE values are those that have been used previously.<sup>6,12,18</sup> The method of representing structural elements is an extension of that used by Benson;<sup>7,8</sup> the first symbol designates the main atom; the succeeding symbols designate the ligands.

Benson treats the *n*-alkanes as strain free and uses a gauche value of 0.8 kcal/mol. Values of other steric terms are derived from generalizations of regularities observed for certain structural features.<sup>7,8</sup> Allinger uses isobutane and neopentane with zero "strain" to define increments for methinyl and quaternary carbons.<sup>13</sup> The disadvantage of this latter definition of standards is that the initial members of a series do not conform to the additivity rules; they are exceptional. (See page 238ff of ref 4).

Fortunately, the FSE values of crowded molecules are not very sensitive to what FSE values are assigned to isoalkanes and to neoalkanes. If the much lower values of 0.30 and 0.60 are used in place of 0.70 and 1.40, FSE values of crowded alkanes are changed by only about 15%. At this point there is no clear advantage for adopting alternative FSE assignments for terminal isoalkanes and for terminal neoalkanes. It is obviously essential to decide on some one appropriate set of standards and on the FSE values to be assigned and to adopt it throughout the study.

**Derivation of *c* Increments.** Tables I and II sum-

(21) Bocian, D. F.; Strauss, H. L. *J. Am. Chem. Soc.* 1977, 99, 2876-82.

(22) DeTar, D. F.; Binzet, S.; Darba, P. *J. Org. Chem.* 1985, 50, 5304-8.

(23) Flamm-Ter Meer, M. A.; Beckhaus, H.-D.; Ruchardt, C. *Therm. Acta* 1986, 107, 331.

(24) Flamm-Ter Meer, M. A.; Beckhaus, H.-D.; Ruchardt, C. *Therm. Acta* 1984, 80, 81.

marize the derivation of  $c$  increments for alkyl groups. The principle used throughout is to make the calculations in sets so that the most fundamental values are least perturbed by uncertainties in the other enthalpy of formation values. The tables summarize the SM values and the FSE values assigned. The  $c$ [C-C-H-H-H-] and  $c$ -[C-C-C-H-H-] values in the footnotes of Table I were determined from the  $n$ -alkanes listed in Table I by a least-squares procedure. These values were then held fixed for all other  $c$ -increment calculations. The  $c$ -[C-C-C-C-H-] and  $c$ [C-C-C-C-C-] values are reported in the footnote of Table II. The  $c$  increments do not differ greatly from published values. The Schleyer values are -10.12, -5.13, -2.16, and -0.30; our earlier values are also similar.

**Experimental FSE Values.** Table III summarizes the FSE values for most of the alkanes and cycloalkanes in the Stull, Westrum, Sinke<sup>4</sup> and in the Pedley-Naylor-Kirby<sup>1-3</sup> collections plus several examples from the literature. The SM values that have been adopted are listed in the tables. For compounds of simple structure, it is possible to estimate FSE values by reference to the FSE values assigned to standards, and these expected values are listed in the last column. For the compounds for which the SM values are not now available, the FBE term is reported but no FSE value has been calculated.

Agreement is close between the values in Table III and those compounds that also appear in Tables VI and VII of the Schleyer reference.<sup>12</sup>

**Consistency Tests.** A number of tests may be made for consistency of the enthalpy of formation data and for the FSE values. These are summarized in Table IV. The first set includes all of the  $n$ -alkanes. Sets 2 and 3 contain all of the isoalkanes and neoalkanes. Set 4 contains all alkanes having an interior methyl group or methyl branches at each end; for these the expected FSE value is 1.40, based on the presence of two gauche interactions and assuming additivity of effects. This expectation is supported by the Wiberg *ab initio* results.<sup>15</sup> The FSE values for cyclohexanes, set 5, and cyclopentanes, set 6, are based on averages of FSE values for those examples that do not have additional steric interactions beyond those due to the rings. These ring values are well defined. Set 7 includes 40 compounds for which standard deviations

**Table IV. Consistency of Experimental FSE Values and Comparison with Expected FSE Values**

set		av exptl FSE	expected FSE	SD of difference <sup>a</sup>
1	28 $n$ -alkanes (average of absolute value)	0.08	0.00	0.13
2	11 isoalkanes	0.64	0.70	0.23
3	7 neoalkanes	1.40	1.40	0.27
4	18 3-methylalkanes (or 2, $n$ -dimethylalkanes)	1.50	1.40	0.27
5	22 cyclohexanes	1.51	(1.40) <sup>b</sup>	0.47
6	16 cyclopentanes	7.56	(7.40) <sup>b</sup>	0.19
7	40 alkanes for which the sd of $\Delta H_f$ is reported, the avg sd of $\Delta H_f$ is 0.37 <sup>c</sup>			0.40 <sup>a</sup>
8	110 alkanes with assigned value of expected FSE			0.42 <sup>a,d</sup>

<sup>a</sup>SD is square root of  $\text{sum}(\text{FSE expected} - \text{FSE experimental})^2/n$ . The assigned FSE of  $n$ -alkanes is 0, of isoalkanes is 0.70, and of neoalkanes is 1.40. Other assignments based on counting gauche interactions. <sup>b</sup>Approximate average of compounds with fewer than about 12 carbons. <sup>c</sup>Square root of the average of the variance. <sup>d</sup>Omitting compounds having a standard deviation of the experimental  $\Delta H_f > 0.8$  kcal/mol.

have been reported for the experimental value of the enthalpy of formation and for which FSE values have been predicted. The average of the variance of these standard deviations corresponds to an average standard deviation of 0.44 while the corresponding average variance based on the differences between the predicted FSE and the experimental FSE gives a standard deviation of 0.42, Table IV; that is, the predicted FSE values are consistent with the experimental estimates. Set 8 reports the average standard deviation for all compounds for which FSE values have been predicted.

The enthalpies of formation come from many sources and have been measured with variable levels of precision. Most of the values reported in the compilations appear to represent remarkably good measurements. But there are occasional serious discrepancies. In many cases discrepancies between different reported values for the same compound can be decided in favor of the value that is consistent with the observed regularities.

## Experimental Formal Steric Enthalpy. 2. Olefins

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Received January 22, 1990

Sets of standard olefins have been selected for defining formal steric enthalpies. All possible olefins can be described in terms of 17 structural elements in addition to the four structural elements used to describe alkanes. It is possible to define definitive FBE increments for 11 of these, and reasonable estimates may be assigned to the rest. For 76 olefins for which FSE values have been assigned or estimated, the standard deviation of the difference between the experimental FSE value and the assigned or estimated value is 0.44 kcal/mol. This value is the same as the reported average uncertainties of the enthalpy of formation data (0.43).

The first paper in this series<sup>1</sup> summarizes the principles of the calculation of experimental values of formal steric enthalpy from enthalpy of formation data.<sup>2-4</sup> Equation

1 defines FSE as the correction to the formal bond enthalpy  $\text{FBE}_{\Sigma n,c}$ , that is needed to reproduce the value

(2) Pedley, J. B.; Rylance, J. *Sussex-N.P.L. Computer Analyzed Thermochemical Data Organic and Organometallic Compounds*; University of Sussex: Sussex, UK, 1977.

(1) DeTar, D. F. *J. Org. Chem.*, previous paper in this issue.