

undergoing two revisions,¹⁴ eq 6 had been proposed for use with phenol and substituted phenols.¹⁵

$$-\Delta H \text{ (kcal/mole)} = 0.0103\Delta\nu_{\text{OH}} \text{ (cm}^{-1}\text{)} + 3.08 \quad (6)$$

Since we intend a full discussion of the $\Delta\nu$ - ΔH relationship subsequently, it will suffice here to test eq 6 rather superficially against some of the data reported in Tables V and VIII. Since eq 6 obviously cannot be used for hydrogen bonds whose enthalpies are less than 3 kcal/mole, we have restricted our comparison between experimental and calculated (eq 6) values (Table XI) to the stronger hydrogen bonds. Even in this re-

stricted range, the average difference between calculated and experimental values is 0.84 kcal/mole. Since the whole range of enthalpies treated is only 5.1 kcal/mole (3.1–8.2 kcal/mole, Table XI), eq 6 is not a very satisfactory method for providing reliable ΔH_f data.⁵⁶

(56) Professor Drago, private communication, has criticized this test of eq 6. As is indicated by footnote *e*, Table XI, some of the bases have more than one hydrogen-bonding site. The use of only the larger $\Delta\nu$ to compute ΔH may lead to inaccuracies. Drago argues that the pure base method may be imprecise, especially with the more polar bases. We concede this possibility, although for DMSO the agreement between calculated and experimental ΔH_f 's is fairly good. We plan a rigorous and direct test of the validity of eq 6, free from these and other objections.

The Evaluation of Strain in Hydrocarbons. The Strain in Adamantane and Its Origin^{1,2}

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Abstract: Many group-increment and bond-energy additivity schemes, *e.g.*, the frequently employed one by Franklin, devised for calculation of heats of formation of acyclic alkanes, are inadequate for cyclic systems. Even those schemes which treat cyclic molecules well are not applicable to the problem of defining hydrocarbon strain energies. Group increments, derived from the heats of formation of the acyclic alkanes in completely skew-free conformations, are presented: CH₃, -10.05 kcal; CH₂, -5.13 kcal; CH, -2.16 kcal; C, -0.30 kcal. These "single-conformation" increments are recommended for the evaluation of strain in hydrocarbons and tables of such strain estimates are provided. A modest strain in cyclohexane (1.35 kcal/mol) and *trans*-decalin (1.79 kcal/mol) is indicated. More important and surprising is the finding of 6.48 kcal/mol of strain in adamantane, thought previously to be a "strain-free" molecule. This strain can be accounted for quantitatively in terms of angle strain and C···C nonbonded repulsions from which the rigidity of adamantane skeleton allows no escape, provided rather hard C···C nonbonded potential functions are employed in computer conformational analysis calculations. Softer C···C nonbonded functions appear to be less satisfactory, as they do not reproduce well the energies and geometries of bridged hydrocarbons. Special cage effects need not be invoked in interpreting the strain in adamantane, nor, presumably, in other bridged polycyclic molecules.

Adamantane has generally been assumed to be a strain-free molecule⁶ since the structural features are thought to be "ideal": all angles are tetrahedral, or nearly so, the bond lengths are normal, and adjacent carbon atoms are held in the staggered, torsionally most favorable conformation.⁷

However, analysis of the recently available thermochemical data for adamantane reveals that adamantane

is, in fact, far from being strain free. This paper establishes this surprising result and provides an interpretation. It is necessary first to define what is meant by "strain" and then to establish the extent to which adamantane is "strained." This involves the estimation of a strain-free heat of formation for adamantane. A critical analysis shows that many of the methods commonly used for estimating such heats of formation have serious flaws which render them inapplicable to cyclic compounds. A new method, free from these defects, is required. Finally, the reason for the unexpected strain in adamantane needs to be found.

Definition of Strain. The concept of strain in organic molecules, although inexact, is conceptually useful. Certain molecules with higher energies than "normal" are found to have distorted structures. This relationship between energy and structure permits a chemist to predict easily which compounds will be strained. For example, molecules with bond angles deviating from the normal values, with atoms approaching each other too closely, or with eclipsed conformations will typically be strained. Since adamantane appears to possess none of these defects, it has long been expected to be strain free.

(1) This work was supported by grants from the National Institutes of Health (AI-07766), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

(2) A preliminary account of this work was presented at the Conference on Stereochemistry, Bürgenstock, Switzerland, May 1967. Some of the calculations have been published in a review.³

(3) J. E. Williams, P. J. Stang, and P. v. R. Schleyer, *Ann. Rev. Phys. Chem.*, **19**, 531 (1968).

(4) National Science Foundation Predoctoral Fellow, 1965–1969; Ph.D. Thesis, Princeton University, 1969.

(5) National Science Foundation Predoctoral Fellow, 1961–1965; Ph.D. Thesis, Princeton University, 1966.

(6) Review: R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(7) Studies of the structure of adamantane: ref 6 and J. Donohue and S. H. Goodman, *Acta Crystallogr.*, **22**, 352 (1967); C. E. Nordman and D. L. Schmitkons, *ibid.*, **18**, 764 (1965). *Cf.* also the structure of diamantane ("congressane"), I. L. Karle and J. Karle, *J. Amer. Chem. Soc.*, **87**, 919 (1965), and of 1-biadmantane, R. A. Alden, J. Kraut, and T. G. Traylor, *ibid.*, **90**, 74 (1968).

Strain is perhaps best defined operationally. Reference molecules are selected which are believed theoretically to be strain free and which have the lowest energies (on some kind of common basis, e.g., for each type of group) observable. For example, we consider a straight chain hydrocarbon in its most stable conformation, a linear zig-zag arrangement, to be the most reasonable basis upon which to base strain estimates for other hydrocarbons. This does not mean that such an alkane is strain free in an absolute sense but only that such a molecule becomes a practical point of reference. It is unlikely that any other hydrocarbons will be found which have lower energies. On this basis, methane, ethane, isobutane, and neopentane, but not 2-methylbutane, are strain free. 2-Methylbutane has an unavoidable skew butane-type interaction which the other molecules do not possess.

However, on this basis a case can be made theoretically that adamantane should not be completely without strain. Angles around carbon with exactly the tetrahedral value of 109.5° are seldom found in nature, and indeed are possible only when carbon is tetrasubstituted with identical groups.⁸ The C-C-C angle in propane⁹ (and in other straight-chain hydrocarbons)¹⁰ is 112.4° , while in isobutane 111.3° is observed.¹¹ Even in cyclohexane, a widening of the ring angles to 111.5° has been found.¹² If it is assumed that the "preferred" or "normal" C-CH₂-C angles are 112.4° , and the C-CH-C angles 111.3° , then adamantane must have some strain, since the cage structure makes the attainment of such angles impossible.⁷ Perhaps also the rigid cage structure accentuates repulsive nonbonded interactions.

Besides the present work,³ quantitative conformational analysis has been reported twice on adamantane. Gleicher and Schleyer¹³ calculated a "total strain" of 1.66 kcal/mol for adamantane, but the basis of reference was different than that being adopted in the present paper. For example, a "total strain" of 0.75 kcal/mol was calculated for isobutane, considered here to be a strain-free molecule. If the Gleicher-Schleyer results are placed on the present basis, adamantane would be essentially strain free also. However, the potential functions used in their paper did not give acceptable results with other bridged hydrocarbons and were really not applicable to the problem at hand.

In their extensive treatment of saturated hydrocarbons by quantitative conformational analysis, Allinger and coworkers¹⁴ included calculations for adamantane. Strain energies were not estimated directly; rather enthalpy correction terms were calculated. This value

for adamantane, 1.42 kcal/mol, was 1.40 kcal greater than that for *trans*-decalin, a strain-free molecule of comparable size. However, there is good reason to believe that Allinger's C...C repulsion potential function is too "soft" (*vide infra*). There are other deficiencies in the Allinger results.

Experimental values for the strain energy depend upon accurate determination of the heat of combustion of gaseous adamantane, as well as upon some method for the accurate calculation of the strain-free value. Although reasonably good estimates of the heat of combustion of solid adamantane have been available,⁶ lack of heat of sublimation data have prevented strain assessments from being made. Two groups have now determined this necessary value, and the results (Table I) are in good agreement.^{15,16} In addition, a highly reliable heat of combustion value of adamantane has recently been established.¹⁶ The thermodynamic data for adamantane have been summarized in Table I.

Table I. Thermodynamic Data for Adamantane at 25°, kcal/mol

$-\Delta H_c^\circ$ (solid)	$\Delta H_{\text{sub}}^\circ$	$-\Delta H_c^\circ$ (gas)	$-\Delta H_f^\circ$ (gas)
(1440.78) ^a			
1440 ^b	14.0 ^c	1426 ^c	33.0 ^c
1439.89 ^d	14.23 ^d	1425.76 ^d	32.94 ^d

^a Estimated indirectly from the heat of combustion of thiaadamantane.⁶ ^b R. J. Wineman, unpublished observation cited in ref 6. ^c Reference 15. ^d Reference 16.

In order to translate these data into an estimate of strain energy of adamantane, recourse must be made to one or more of the many schemes available for the calculation of heats of atomization, heats of combustion, or heats of formation of hydrocarbons. Since these three heats are directly related, such calculations give directly comparable results for strain energies, which are defined as the difference between calculated and observed values. The calculation methods available have been summarized and discussed in reviews.¹⁷⁻²⁰ Briefly, there are two approaches; one is based on bond energies and the second, which may or may not be equivalent depending on the assumptions involved, is based on group increments. Bratton, Szilard, and Cupas used three of the bond-energy

Table II. Calculated Strain Energies of Adamantane^a

Strain energy	Method of calculation ^b		
	Allen-Skinner	Tatevskii	Laidler
	3.3	-2.1	0.4

^a See ref 15; in kcal/mol. ^b References 17-19.

(15) W. K. Bratton, I. Szilard, and C. A. Cupas, *J. Org. Chem.*, **32**, 2019 (1967).

(16) E. F. Westrum, Jr., private communication; cf. "Bulletin of Thermodynamic and Thermochemistry," No. 11, E. F. Westrum, Jr., Ed., University of Michigan, 1968, p 14.

(17) H. A. Skinner and G. Pilcher, *Quart. Rev. (London)*, **17**, 264 (1963).

(18) G. R. Somayajulu, A. P. Kudchadker, and B. J. Zwolinski, *Ann. Rev. Phys. Chem.*, **16**, 213 (1965).

(19) G. J. Janz, "Thermodynamic Properties of Organic Compounds," Academic Press, New York, N. Y., 1967.

(20) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(8) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 10-13.

(9) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960), and references cited therein.

(10) K. Kuchitsu, *Bull. Chem. Soc. Jap.*, **32**, 748 (1959); R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959); R. A. Bonham, L. S. Bartell, and D. A. Kohl, *ibid.*, **81**, 4765 (1959); N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1747 (1961). Also see T. Ukaji and R. A. Bonham, *J. Amer. Chem. Soc.*, **84**, 3627 (1962); F. A. Momany, R. A. Bonham, and W. H. McCoy, *ibid.*, **85**, 3077 (1963).

(11) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960); cf. G. H. Pauli, F. A. Momany, and R. A. Bonham, *J. Amer. Chem. Soc.*, **86**, 1286 (1964).

(12) V. A. Atkinson, *Acta Chem. Scand.*, **15**, 599 (1961); V. A. Atkinson and O. Hassel, *ibid.*, **13**, 1737 (1959); M. Davis and O. Hassel, *ibid.*, **17**, 1181 (1963).

(13) G. J. Gleicher and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(14) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968).

Table III. Heat of Formation Group Increments^a

Group	Franklin ^b	Souders, Matthews, and Hurd ^c	Benson and Buss ^d	This work, "skew separate"	This work, "single conformation"
CH ₃	-10.12	-10.05	-10.08	-10.12	-10.05
CH ₂	-4.926 ^e	-4.95 (acyclic) -4.91 (6 ring)	-4.95	-4.93	-5.13
CH	-1.09 ^{e,f}	-1.57 ^g (acyclic) -1.53 ^g (6 ring) -0.88 ^h (acyclic)	-1.48 ^f -1.90 ^k	-2.11 ^k	-2.16
C	+1.07 ^{e,f}	+0.85 ⁱ +2.45 ⁱ	+1.95 ^f +0.50 ^k	-0.23 ^k	-0.30
Skew corrections		+0.69 (CH, acyclic) ^f +0.65 (CH, 6 ring) ^f -0.80 (C, acyclic) ^f	+0.70 (acyclic) +0.80 (general acyclic + cyclic) ^m	+0.67 (acyclic) +0.97 (6 ring, axial)	+0.70 (acyclic)

^a Gas phase, 25°, kcal/mol. ^b Reference 22. ^c Reference 23. ^d Reference 24. ^e A correction of -0.45 kcal to be added for C₆ rings. ^f Average values, including skew interaction corrections. ^g For use when the branch is on the second carbon of a chain; *i.e.*, includes a correction for *one* skew interaction. ^h For use when the branch is on the third or higher carbon on a chain; *i.e.*, includes a correction for *two* skew interactions. ⁱ Branch on second carbon. Includes a correction for *two* skew interactions. ^j Branch on third or higher carbon. Includes a correction for *four* skew interactions. ^k For use only when skew interactions will be made separately. ^l Not evaluated by the original authors,²³ but calculated from their data. ^m Reference 20.

schemes from the literature to estimate the strain energy of adamantane, concluding "It is evident from the figures in Table II that adamantane possesses a small strain energy."¹⁵

It is our contention that a more detailed analysis of this type of calculation leads rather to the conclusion that an appreciable strain energy of about 6 kcal/mol is indicated for adamantane. In order to establish this point it will be necessary to critically evaluate the existing method of evaluating strain energies, to propose modifications, and to apply the modified scheme to polycyclic hydrocarbons. It will be made clear that the behavior of adamantane deviates significantly from that of other molecules expected from theory to be strain free.

Evaluation of Group Increments. Although both bond-energy and group-increment approaches are capable of refinement to the point where excellent agreement with literature values can be achieved,¹⁷⁻²⁰ we prefer the use of group increments. This method is simpler and less artificial in its final application, and can be cast into a framework based on principles of conformational analysis.

When a long chain *n*-alkane (C₆ and above) is increased by one methylene group, the heat of formation changes by -4.93 kcal/mol.²¹ This value remains constant for further such additions, and is independent of the nature of a group, such as phenyl, cyclopentyl, etc., at the end of a long chain.¹⁷⁻²⁰ In a higher *n*-alkane, assuming each methylene contributes the same increment, -4.93 kcal, to the heat of formation, the methyl groups are found to contribute -10.12 kcal/mol each. The various literature group increment schemes, those of Franklin,²² Souders, Matthews, and Hurd,²³ and Benson and Buss,^{20,24} and our own "skew-separate" agree well on these choices (Table III).

The group increments proposed for CH (trisubstituted carbon) and for C (tetrasubstituted carbon) upon first

examination (Table III) show considerable variation. Upon analysis, some of these apparent discrepancies prove to be illusory; they arise because of the different mathematical procedures used in formulating the various schemes.

Franklin,²² after evaluating the CH₂ and CH₃ increments from data on straight-chain hydrocarbons by the method described above, treated the remainder of the API hydrocarbons²¹ in a statistical manner to obtain CH and C increments. Only in the case of highly branched alkanes were correction terms introduced, and this was done in an artificial way, *e.g.*, adjacent quaternary C's were assigned a correction factor of 5.0 kcal. (In conformational terms this situation would be equivalent to six skew interactions.)²⁵ Except for isobutane and neopentane, the introduction of a branch in any acyclic hydrocarbon introduces skew interactions (equivalent to the skew conformation of *n*-butane) which increase the enthalpy content. These skew interactions were not explicitly considered by Franklin, and his CH and C increments are more positive due to the inclusion of these skew interactions into the averages. Unfortunately, this limitation is not appreciated by many authors who have used the Franklin scheme to estimate strain energies in molecules (especially cycloalkanes) where the Franklin group increments are expected to give poor results.

Cyclic compounds with six-membered rings have not generally been included^{17,18} in the evaluation of the various calculation schemes. For the purposes of the analysis of strain in adamantane, use of comparison molecules with structures as closely related as possible is desirable. For such test purposes, the molecules methylcyclohexane, *cis*-1,3- and *trans*-1,4-dimethylcyclohexane,²¹ *trans*-decalin,²⁶ and *trans-syn-trans*-perhydroanthracene²⁷ were chosen, and the results from several schemes are summarized in Table IV.

These test molecules, like adamantane, are free of the type of skew interaction found in acyclic molecules in

(21) American Petroleum Institute, Project 44, "Selected Values of the Thermodynamic Properties of Hydrocarbons," Carnegie Institute of Technology, Pittsburgh, Pa., 1952 onwards; M. C. Loeffler and F. D. Rossini, *J. Phys. Chem.*, **64**, 1530 (1960).

(22) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(23) M. Souders, Jr., C. S. Matthews, and C. O. Hurd, *ibid.*, **41**, 1048 (1949).

(24) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958).

(25) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965.

(26) T. Miyazawa and K. S. Pitzer, *J. Amer. Chem. Soc.*, **80**, 60 (1958).

(27) J. L. Margrave, M. A. Frisch, R. G. Bautista, R. L. Clarke, and W. S. Johnson, *ibid.*, **85**, 546 (1963).

Table IV. Experimental and Calculated $-\Delta H_f^\circ$ (g) (kcal/mol) for Strain-Free Test Molecules with CH Groups and Adamantane

Method	2m3	mc6	cis-13mc6	trans-14mc6	trans-Decalin	trans-syn-trans-Perhydroanthracene	Av dev ^a	Adamantane
Exptl	32.15 ^b	36.99 ^b	44.16 ^b	44.12 ^b	43.57 ^c	58.13 ^d		32.94
Franklin ^e	31.45 (0.70)	36.31 (0.68)	42.59 (1.57)	42.59 (1.53)	42.52 (1.05)	55.01 (3.12)	+1.35 ± 1.06	34.67 ⁿ -1.73
Laidler ^f	31.48 (0.65)	35.39 (1.60)	41.78 (2.38)	41.78 (2.34)	40.85 (2.72)	52.72 (5.41)	+2.44 ± 1.08	33.40 -0.46
Tatevskii ^g	32.27 (-0.12)	35.79 (1.20)	41.82 (2.34)	41.82 (2.30)	38.98 (4.59)	48.44 (9.69)	+3.33 ± 2.00	30.96 +1.98
Somayajulu, Zwolinski ^h	32.07 (0.08)	38.38 (-1.39)	44.84 (-0.68)	44.84 (-0.72)	43.19 (0.38)	54.38 (3.75)	+0.21 ± 1.24	34.94 -2.00
Allen-Skinner ⁱ	32.13 (0.02)	36.54 (0.45)	43.50 (0.66)	43.50 (0.62)	42.98 (0.59)	56.20 (1.93)	+0.71 ± 0.41	36.52 -3.58
Kalb, Chung, Allen ^j	32.03 (0.12)	36.81 (0.18)	43.72 (0.44)	43.72 (0.40)	43.52 (0.05)	57.14 (0.99)	+0.36 ± 0.25	37.22 -4.28
Benson, Buss ^k	32.05 (1.00)	36.73 (0.26)	43.76 (0.40)	43.76 (0.36)	43.40 (0.17)	57.10 (1.03)	+0.39 ± 0.22	37.30 -4.36
Souders, Mathews, Hurd ^l	32.37 (-0.22)	36.78 (0.21)	44.10 (0.06)	44.10 (0.02)	43.64 (-0.07)	57.82 (0.31)	+0.05 ± 0.14	38.18 -5.24
Skew-separate	32.46 (-0.31)	36.88 (+0.12)	44.18 (-0.02)	44.18 (-0.06)	43.66 (-0.09)	57.74 (+0.39)	0.00 ± 0.16	38.02 -5.08
Single-conformation ^m	32.31 -0.16	36.86 -0.87	44.94 -0.78	44.94 -0.82	45.36 -1.79	59.94 -1.81	Not applicable	39.42 -6.48

^a Average of values in parentheses which are the differences: ΔH_f° (calcd) - ΔH_f° (exptl). ^b Reference 21. ^c Reference 26. ^d Reference 27. ^e Includes a correction of -0.45 kcal for each 6 ring; ref 22. ^f K. J. Laidler, *Can. J. Chem.*, **34**, 626 (1956); E. G. Lovering and K. J. Laidler, *ibid.*, **38**, 2367 (1960). ^g V. M. Tatevskii, V. A. Benderskii, and S. S. Yarovoi, "Rules and Methods for Calculating the Physicochemical Properties of Paraffinic Hydrocarbons," B. P. Mullins, Ed., Pergamon Press, New York, N. Y., 1961. ^h H. R. Somayajulu and B. J. Zwolinski, *Trans. Faraday Soc.*, **62**, 2327 (1966). ⁱ Reference 17; T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959); H. A. Skinner, *J. Chem. Soc.*, 4396 (1962). ^j A. J. Kalb, A. L. H. Chung, and T. L. Allen, *J. Amer. Chem. Soc.*, **88**, 2938 (1966). ^k Reference 24. ^l Reference 23; calculated using modified CH increments (see text) for compounds in which no skew interactions are present. The value used was 2.18 kcal (6 ring), obtained by adding -0.65 kcal (skew interaction correction, 6 ring) to S-M-H's 6-ring CH increment of -1.53 kcal (Table III). ^m ΔH_f° estimates are not on the same basis as those of preceding methods. The values in the second line are strain estimates derived from the use of single conformations of acyclic hydrocarbons as the strain-free basis. See text. ⁿ Correction used was $10/6 \times -0.45 = -0.75$, for there are 10 cyclohexanoid carbons in adamantane.

which H...H repulsions dominate in the determination of conformational energies and equilibria. In the C₄-C₆ rings, geometrical requirements greatly reduce possibilities for significant H...H interactions. Although the ring carbons of chair cyclohexane are in skew conformations, these are not comparable to the skew conformations in acyclic molecules, because of the removal of the dominant H...H repulsions. Thus, no skew corrections are applied to the test molecules of Table IV. However, even cyclohexanoid molecules may not be strain-free, because C...C interactions across the ring may be significant. These C...C interactions of the 1,3 and gauche 1,4 type are both undoubtedly repulsive³ and contribute to the flattening of the cyclohexane ring from the "ideal" 109.5° chair geometry.^{12,28} Since adamantane is built up of chair-form cyclohexane rings, it becomes necessary to have cyclohexanoid comparison molecules. If energies can not be computed well for these models, little confidence can be placed in the values obtained for adamantane.

Franklin's increments give unacceptable results, even when full correction factors for ring compounds are included (Table IV). The deviations are to be expected. H...H repulsions are relatively minor in the test molecules, and Franklin implicitly includes skew interaction energies, which are dominated by H...H repulsions, in his increments. Adamantane is also without large H...H repulsions, and Franklin's method is not satisfactory for strain estimation.

Laidler's scheme,²⁹ although based on bond energies,

(28) R. A. Wohl, *Chimia*, **18**, 219 (1964).

(29) See Table IV, footnote f.

is equivalent to Franklin's in approach, in the assumptions, and very nearly in the results. C-C bond energies are considered to be constant, but different bond energies are given for C-H bonds attached to primary, secondary, and tertiary carbons. No corrections for any skew interactions are explicitly involved. Rather, these corrections are averaged into the statistical treatment of the data. It is easy to convert Laidler's bond energies into group increments. For example, the methyl group increment would be $3 \times 3.45 (E_{CH(p)}) - 0.225 (1/2 E_{CC}) = -10.125$ kcal/mol; similarly, CH₂ = -4.83, CH = -1.105, and C = +0.90. These values are close to those of Franklin (compare Table III), but they are in no way applicable to the adamantane strain problem because of the same basic inherent defects (see Table IV).

The method of Souders, Mathews, and Hurd²³ represents a further refinement, since skew interactions are included implicitly in their treatment. In the evaluation of increments for CH and C groups, the position of attachment of these groups along a hydrocarbon chain was taken into account, and different values were proposed to apply to these situations (see Table III). A methyl group at C₂ of a paraffin of four or more carbons has one skew interaction, while a C₃ methyl (five or more carbon atoms) has two skew interactions. Similarly, a 2,2-dimethyl group has two and a 3,3-dimethyl four skew interactions. For more highly branched systems, further correction terms were proposed, in a manner similar to Franklin's. Although Souders, Mathews, and Hurd did not think in terms of skew interactions, skew correction factors can easily be

calculated from their data. The difference between a C₂ and a C₃-CH branch value is 0.69 kcal/mol, and this represents the value of a skew interaction (Table III). Since their CH increment for a C₂ branch situation contains implicitly one skew interaction, a more reasonable CH increment would be $-1.57 - 0.69 = -2.26$ kcal. It is this value which properly should be used in calculation of the heat of formation of molecules without the skew interactions found in rings, such as *trans*-decalin, 1,3-*cis*- and 1,4-*trans*-dimethylcyclohexane, and *trans-syn-trans*-perhydroanthracene. For these molecules, reasonable results are obtained using this modification; poorer results without (Table IV). It is this modification which also should be used for calculation of the strain energy of adamantane.

Benson and Buss^{20,24} appear to have been the first to use the method which we favor. A set of group increments were presented equivalent to Franklin's, but also a second set of alternative values were proposed for use with skew interaction corrections. The number of skew interactions can be determined readily from a conformational analysis of the molecule in question. Not only is there an appreciable gain in simplicity, since a large number of specific "corrections" for different situations do not have to be invoked, but excellent agreement with observed data is also achieved. Only with the most highly branched and congested molecules, where difficulties are most to be anticipated, are significant errors encountered, and even these are not large. It is this set of increments for use with skew corrections which is applicable to the calculation of strain energy of adamantane (Table IV).

We endorse and follow Benson and Buss. Our skew-separate increments differ but slightly from theirs, and only significantly in the C values (Table III). The CH₃ and CH₂ values were evaluated from straight-chain hydrocarbons of moderate length (see above). The average difference in heats of formation between 2-methyl- and 3-methylalkanes gives a direct estimate of the energy of a skew interaction. Using this correction, CH increments were evaluated from data²¹ on methyl-substituted alkanes. Reasonable agreement is found between the value thus derived of -2.11 kcal/mol, Benson and Buss's of -1.90 kcal, and the calculated value of -2.26 kcal from Souders, Matthews, and Hurd's data. Less agreement is found between the three C increment estimates (Table III; the value from the S-M-H data is $0.85 - 2(0.69) = -0.53$ kcal).

Other Schemes. The derivation of the Tatevskii scheme has been described in the original³⁰ and in the review literature.^{17,18} In the final form, nine parameters are needed for alkane heat of formation calculations, and these parameters were evaluated by the "statistical" method; hence skew interactions are averaged into the various parameters. The method works very well for the acyclic alkanes,^{17,18,30} but fails badly for cyclic hydrocarbons (Table IV). The calculation of a "negative" strain in adamantane (Table II) is a further illustration of the failure of this method.

The Somayajulu-Zwolinski method³¹ is one of the most complicated of all, but it was devised to reproduce the data for even the most highly branched and congested acyclic (but not cyclic) hydrocarbons. Un-

acceptable results are obtained for the test molecules of Table IV.

Allen's scheme,³² as modified by Skinner,^{17,33} is a fairly satisfactory bond-energy approach. Here, also, corrections for skew interactions are employed, and Skinner, instead of assuming a constant value for such skew interactions, proposed a whole set of values for use in various situations. We would prefer to employ a constant value based on simple model compounds. Deviations from calculated values in the more congested systems would then be regarded as strain. Of course, Skinner's modification should give more accurate agreement with experiment, and this can be a worthwhile goal, but at the expense of increased complexity and loss of interpretive significance. We have followed Skinner in one important particular. Methyl groups axial to a cyclohexane ring are well known to have higher skew interaction values than their acyclic counterparts,²⁵ due to fewer degrees of freedom for strain relief. A separate value for skew interactions of axial methyl groups has been included in Table III. The skew interaction value of the methyl group in 2-methyladamantanes should be even higher than the axial cyclohexane value, because of the still more limited strain relief mechanisms present in such rigid and constrained molecules.

Further improvement has been achieved by the modification proposed by Kalb, Chung, and Allen.³⁴ Results virtually identical with those of the Benson-Buss scheme are found with the test molecules of Table IV and virtually the same strain energy 4.28 *vs.* 4.36 kcal/mol is calculated for adamantane.

Allinger, *et al.*,¹⁴ have also presented a simple bond-energy scheme, which, however, was developed and must be used in conjunction with corrective terms supplied by their conformational calculations. The estimated ΔH_f^\ddagger of adamantane, -34.62 kcal/mol, is rather close to the experimental value, -32.94 kcal/mol. However, analyses of the Allinger results show that they are conspicuously unreliable for other cage molecules, norbornane and bicyclo[2.2.2]octane (Table V), and this renders suspect the adamantane result.³⁵

Both the Benson-Buss and Kalb-Chung-Allen methods gave average values for the test molecules in Table IV somewhat more positive than the experimental ones. If the calculated strain values for adamantane are corrected accordingly, estimates near 5 kcal will be obtained. The best of the group increment schemes (Table IV) also indicate a strain of that magnitude for adamantane: 5.24 kcal/mol (Souders, Matthews, and Hurd) and 5.08 kcal/mol (our own skew-separate scheme). Thus the best available calculation methods agree that there is appreciable strain in adamantane, about 5 kcal/mol, while other analogous cyclohexanoid molecules (Table IV) are essentially strain free, on the same basis. This conclusion is more reliable than that reached from the calculations summarized in Table I.

Single-Conformation Group Increments. It should be clear that even methods such as the Benson and Buss or our skew-separate one cannot be thought to give truly strain-free estimates of heats of formation even

(32) See Table IV, footnote *i*.

(33) See Table IV, footnote *i*.

(34) See Table IV, footnote *j*.

(35) Our published quantitative conformational analysis results with such cage molecules were even more unreasonable energetically.¹³

(30) See Table IV, footnote *g*.

(31) See Table IV, footnote *h*.

Table V. Analysis of the Allinger Calculation^a for Cage Molecules

	Norbornane	Bicyclo- [2.2.2]- octane	Adaman- tane
$-\Delta H_f(\text{g})$ exptl	12.42 ^b (8.4), ^c (15.8) ^d	24.09 ^e	32.94
$-\Delta H_f(\text{g})$ calcd ^a	16.2	17.55	34.62
Difference	3.8	-6.54	1.68

^a Reference 14. ^b Based on the heat of formation of the solid, -22.01 kcal/mol (A. F. Bedford, A. E. Beezer, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3823 (1963)), and a sublimation heat of 9.59 kcal/mol (R. H. Boyd, private communication). ^c Estimated by R. B. Turner, P. Goebel, B. J. Mallon, W. v. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, 90, 4315 (1968). ^d Allinger's estimate. This value is in error due to the use of a value of the heat of vaporization, 2.2 kcal/mol,¹ incorrectly calculated from Trouton's rule where °K and not °C should be used. ^e Based on the experimental heat of formation of the solid hydrocarbon, -35.15 kcal/mol (E. F. Westrum, Jr., and S. S. Wong, to be published; S. S. Wong, Ph.D. Thesis, University of Michigan, 1966), and a heat of sublimation of 11.06 ± 0.20 kcal/mol (R. H. Boyd, private communication).

after removal of the skew-interaction corrections. Of course, no hydrocarbon is really strain free, in the sense of having no repulsive intramolecular interactions. The acyclic alkanes in their completely staggered, transoid conformations approach the ideal most closely. At equilibrium, however, such hydrocarbons in the gas phase are necessarily a mixture of conformers, in some of which skewed arrangements will be present. This is because the enthalpy differences between conformations are often too small to ensure that only one form will be present. Also, entropy often favors the less stable conformations. To obtain heats of formation and group increments, as free as possible from the effects of strain, corrections should be made for these residual skew interactions. In other words, single-conformation group increments referring only to a single strain-free conformation are needed.

Allinger¹⁴ has performed his calculations on single conformations. However, even after correction for conformational strain (due to residual skew conformations) straight-chain alkanes still have an excess calculated repulsive interaction. Since Allinger's bond-energy scheme is devised to compensate for such repulsive interaction, it is not generally applicable.

Straightforward application of the Boltzmann distribution law gives the population of each conformer. Mann³⁶ has tabulated the results of such treatment for many acyclic alkanes, assuming a skew-interaction energy of 0.7 kcal/mol, in good agreement with the value we derived above. The single-conformation increments in Table VI were computed from heats of formation corrected using Mann's data.³⁶ The only appreciable difference between the single-conformation and the skew-separate increments is in the value for CH₂ (see Table III). This is to be expected: addition of a methylene greatly increases the number, and hence statistical probability, of conformations having skew arrangements. Addition of CH or C groups, on the other hand, in general increases the number of "built-in" skew interactions, present in all conformations and hence of the sort removed by the analysis giving skew-separate increments.

(36) G. Mann, *Tetrahedron*, 23, 3375, 3393 (1967); G. Mann, M. Mühlstädt, J. Braband, and E. Döring, *ibid.*, 23, 3393 (1967).

Table VI. Derivation of Single Conformation Increments

Molecule ^b	Z _g ^c	$-\Delta H_f(\text{exptl})^d$	$-\Delta H_f(\text{calcd})^e$	Deviation	Strain ^f
Compounds used in computing the single conformation increments of Table III ^a					
-4	0.380	30.15	30.10	-0.05	0.22
2M-3	0.000	32.15	32.32	0.17	0.17
-5	0.659	35.00	35.04	0.04	0.50
2M-4	1.130	36.92	36.66	-0.26	0.53
22M-3	0.000	40.27 ^g	40.50	0.23	0.23
-6	0.950	39.96	39.97	0.01	0.68
2M-5	1.310	41.66	41.67	0.01	0.93
3M-5	2.290	41.02	40.98	-0.04	1.56
22M-4	2.000	44.35	44.24	-0.11	1.29
-7	1.250	44.89	44.90	0.01	0.89
2M-6	1.640	46.60	46.57	-0.03	1.12
3M-6	2.470	45.96	45.99	0.03	1.76
3E-5	3.580	45.34	45.21	-0.13	2.38
22M-5	2.000	49.29	49.37	0.08	1.48
24M-5	2.000	48.30	48.27	-0.03	1.37
33M-5	4.000	48.17	47.97	-0.20	2.60
-8	1.552	49.82	49.82	0.00	1.09
2M-7	1.930	51.50	51.50	0.00	1.35
3M-7	2.790	50.82	50.90	0.08	2.03
4M-7	2.650	50.69	51.00	0.31	2.17
3E-6	3.750	50.40	50.23	-0.17	2.46
24M-6	3.230	52.44	52.54	0.10	2.36
25M-6	2.340	53.21	53.16	-0.05	1.59
Other acyclic alkanes not used in the increment determination					
-2	0.000	20.24	20.10	-0.14	-0.14
-3	0.000	24.82	25.23	0.41	0.41
23M-4	2.380	42.49	42.87	0.38	2.05
23M-5	3.550	47.62	47.18	-0.44	2.05
223M-4	4.000	48.96	49.92	0.96	3.76
22M-6	2.380	53.71	54.24	0.53	2.20
23M-6	3.740	51.13	52.18	1.05	3.67
33M-6	4.000	52.61	53.10	0.49	3.29
2M3E-5	5.000	50.48	51.30	0.82	4.32
3M3E-5	6.000	51.38	51.70	0.32	4.52
223M-5	5.000	52.61	54.35	1.74	5.24
224M-5	4.500	53.57	54.70	1.13	4.28
223M-5	6.000	51.73	53.65	1.92	6.12
2233M-4	6.000	53.99	56.70	2.71	6.91
33E-5	8.00	55.44 ^h	55.44	0.00	5.60
2233M-5	8.00	56.70 ^h	60.43	3.73	9.33
2234M-5	6.38	56.64 ^h	60.46	3.82	8.29
2244M-5	4.00	57.83 ^h	63.23	5.40	8.20
2334M-5	8.00	56.46 ^h	59.33	2.87	8.47

^a Energies in kilocalories per mole. Increments computed by computer least-squares minimization from data for 23 molecules containing a total of 152 carbon atoms. ^b Notation adapted by Allen from Platt.³⁴ ^c Average number of *gauche* interactions per molecule, taken from ref 36 or calculated by similar procedures. ^d Experimental heats of formation from ref 21 unless otherwise indicated. ^e $-\Delta H_f(\text{calcd})$ = sum of increments + 0.7 Z_g. ^f Strain is the difference between $\Delta H_f(\text{exptl})$ and the sum of the group increments. ^g G. Pilcher and J. D. M. Chadwick, *Trans. Faraday Soc.*, 63, 2357 (1967). ^h A. Labbauf, J. B. Greenshields, and F. D. Rossini, *J. Chem. Eng. Data*, 6, 261 (1961).

In Table VI we list the compounds used in deriving the single conformation group increments and other acyclic compounds not used in the derivation. For the latter, the difference between experimental and calculated heats of formation is a measure of the deviation from increment additivity or of the nonconstancy of skew interactions due to excessive crowding and 1,5-methyl-methyl interactions. As expected, compounds such as 2,2,3,3-tetramethylbutane show considerable deviation, indicative of such severe crowding.

The expectation that 1,4-CC interactions in cyclohexane are repulsive is borne out by the calculation of modest strain energies for the test molecules in Table

IV. Cyclohexane itself is found to be strained by 1.35 kcal/mol. Using the force constants of Snyder and Schachtschneider³⁷ and a torsional barrier of 3.0 kcal/mol, the angle and torsional strain in cyclohexane is computed to be 0.65 kcal/mol. At least half the strain in cyclohexane thus comes from nonbonded repulsions, the bulk of them C···C.

For computing strain energies, we believe the single-conformation increments to be the proper choice. However, if it is desired to reproduce heats of formation for molecules having relatively uncrowded structures, Table IV shows that our skew-separate increments give excellent results.

Table VII presents a compilation of our estimates for the strain energies, based on the single-conformation increments, for hydrocarbons for which data are available in the literature. We believe our values to be superior to earlier estimates. Of course, in compiling these estimates, corrections for skew interactions were *not* included; such interactions are often important in contributing to the total strain. Such strain estimates are also included in Tables IV and VI.

Discussion

Adamantane is found to possess 6.5 kcal/mol of strain relative to the acyclic hydrocarbons in skew-free conformations. Relative to *trans*-decalin, another cyclohexanoid molecule with a comparable number of carbon and hydrogen atoms, adamantane is strained by 4.7 kcal/mol using single-conformation increments or 5.0 kcal/mol using skew-separate increments (Table IV). These are surprising and noteworthy results, for adamantane might be expected from theory to be strain free.

It is possible that the finding of strain in adamantane is the result of some inherent deficiency in the group-increments method. Strictly speaking, the energies of groups or of bonds are not independent of their environments, *e.g.*, the energy of a C–H bond should depend not only on the substitution type of the carbon but on the nature of the other substituents on carbon as well. As one proceeds down a homologous series, such as the *n*-alkanes, however, it is reasonable to expect that constancy in increment energies should be, and is, eventually reached. Group and bond additivity schemes take advantage of this fact, and many, even the simplest, work very well. Adamantane, unlike the molecules to which these additivity schemes are generally applied, has a very globular shape. It is conceivable that within the rigid adamantane cage special interactions, not found in less congested systems, take place. Such interactions cannot be too important, however, because the strain in adamantane can be rationalized using the methods of conventional conformational analysis.

Sources of Strain in Adamantane. It is clear that adamantane should not be completely without strain, for the two reasons mentioned above. In the first place, because of geometrical restrictions, the CCC angles in adamantane cannot attain the values of 112.4° for C–CH₂–C^{9,10} and 111.3° for C–CH–C¹¹ found in the acyclic alkanes in their strain-free conformations. Using the force constants of Snyder and

Schachtschneider,³⁷ a CCC angle strain of 1.8 kcal/mol is computed. Small CCH and HCH deformations, caused in part by H···H repulsions across the faces of the adamantane tetrahedron, bring the total angle strain to 2.3 kcal.

Secondly, there should be appreciable repulsive C···C interactions in the adamantane skeleton. Using strain-free increments cyclohexane was found to possess 1.35 kcal of strain, about half of which comes from nonbonded interactions. Of these the C···C interactions are repulsive, but there are many long C···H distances and even a moderately “hard” function such as that of Bartell³⁸ gives a sizable attractive C···H energy. The H···H energy is probably repulsive and predicted to be small by any but the very “hardest” of H···H functions.³

Each of the faces of the adamantane tetrahedron is a cyclohexane ring, so that cyclohexyl C···C repulsions will be quadrupled in adamantane. Quantitative conformational analysis, using the functions of Bartell,³⁸ show that the C···H attractions are only doubled, as are the H···H repulsions. Comparison with *trans*-decalin, a molecule with molecular formula comparable to that of adamantane, is instructive. In *trans*-decalin the repulsions present in cyclohexane are approximately doubled, but six new 1,4-C···C interactions, of the type found between terminal carbons of *transoid n*-butane, are introduced. These interactions are most certainly attractive. They are also found in methylcyclohexane, and as the methylcyclohexane strain is less than that in cyclohexane (0.89 *vs.* 1.35 kcal/mol), so the *trans*-decalin strain is much less than twice that of cyclohexane (1.79 *vs.* 2(1.35) = 2.70 kcal/mol, Table IV, single-conformation increments).

In order to illustrate some of these points, we have performed strain-energy computations using the program described previously^{3,13} with various potential functions chosen from the literature (Table VIII). Unfortunately, most potential functions which have been suggested for conformational analysis are derived from properties dominated by H···H interactions, *e.g.*, intermolecular interactions between saturated alkanes, the axial–equatorial methylcyclohexane difference, etc. C···C functions from such data are likely to be underdetermined and wholly inappropriate. The force field developed by Allinger and coworkers,¹⁴ quite successful for many hydrocarbons, greatly underweights C···C repulsions. The clearest indications of this are the structures and energies (Table V) calculated for some common cage molecules. The calculated heat of formation for adamantane does not agree very well with the experimental value, but for norbornane and bicyclo[2.2.2]octane agreement is particularly poor (Table V). Experimentally, X-ray and electron-diffraction values for the CC bond lengths in adamantane,^{6,7} norbornane,³⁹ and bicyclo[2.2.2]octane⁴⁰ are 1.532–1.542, 1.544–1.561, and 1.51–1.55 Å, respectively,

(38) L. S. Bartell, *J. Chem. Phys.*, **32**, 827 (1960).

(39) G. Dallinga and L. H. Toneman, *Rec. Trav. Chim. Pays-Bas*, **87**, 795 (1968); J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968)), have also criticized the Allinger results.

(40) Value is for C₂–C₃ length of 1,4-bicyclo[2.2.2]octane derivatives: O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968); A. F. Cameron, G. Ferguson, and D. G. Morris, *J. Chem. Soc., B*, 1249 (1968); R. Destro, G. Filippini, C. M. Gramacciolli, and M. Simonetta, *Tetrahedron Lett.*, 2493 (1969).

(37) R. G. Snyder and J. H. Schachtschneider, *Spectrochim. Acta*, **21**, 169 (1965).

Table VII. Strain Estimates Based on Single Conformation Increments (kcal/mol)

Compound	ΔH_f° (exptl)	ΔH_f° (calcd)	Strain	Compound	ΔH_f° (exptl)	ΔH_f° (calcd)	Strain
Cycloalkanes ^b				Cyclo- and Polycycloalkenes ^c			
Cyclopropane	12.74 ^a	-15.40	28.13	Cyclopropene	66.6 ^a	+12.1	54.5
<i>cis</i> -1,2-Dimethylcyclopropane	1.3 ^b	-29.55	30.85	1-Methylcyclopropene	58.2 ^a	+3.7	54.5
Ethylcyclopropane	1.1 ^b	-27.60	28.7	1,2-Dimethylcyclopropene	46.4 ^b	-4.6	51.0
Cyclobutane	6.38 ^{a,c}	-20.52	26.90	Methylenecyclopropane	48.0 ^a	6.3	41.7
Methylcyclobutane	-0.6 ^a	-27.6	27.0	2-Methylmethylenecyclopropane	39.4 ^b	-0.7	40.1
Cyclopentane	-18.46 ^a	-25.65	7.19	Ethylidenecyclopropane	36.1 ^b	-1.4	37.5
Methylcyclopentane	-25.50 ^a	-32.73	7.23	Cyclobutene	37.5 ^b	6.9	30.6
1,1-Dimethylcyclopentane	-33.05 ^a	-40.92	7.87	1-Methylcyclobutene	28.3 ^b	-1.4	29.7
<i>cis</i> -1,2-Dimethylcyclopentane	-30.96 ^a	-39.81	8.85		29.1 ^a		30.5
<i>trans</i> -1,2-Dimethylcyclopentane	-32.67 ^a	-39.81	7.14	1,2-Dimethylcyclobutene	19.8 ^b	-9.8	29.6
<i>cis</i> -1,3-Dimethylcyclopentane	-32.47 ^a	-39.81	7.34		20.8 ^a		30.6
<i>trans</i> -1,3-Dimethylcyclopentane	-31.93 ^a	-39.81	7.88	Methylenecyclobutane	30.0 ^a	1.2	28.8
Ethylcyclopentane	-30.37 ⁱ	-37.86	7.59	1,3-Dimethylenecyclobutane	53.3 ^a	22.9	30.4
<i>n</i> -Propylcyclopentane	-35.93 ⁱ	-42.99	7.60	1-Methyl-3-methylenecyclobutene	48.3 ^a	20.3	28.0
Cyclohexane	-29.43 ^a	-30.78	1.35				
1,1-Dimethylcyclohexane	-43.26 ^a	-46.05	2.79	Cyclopentene	8.56 ^a	1.8	6.8
<i>cis</i> -1,2-Dimethylcyclohexane	-41.15 ^a	-44.94	3.79	1-Methylcyclopentene	-1.5 ^a	-6.5	5.0
<i>trans</i> -1,2-Dimethylcyclohexane	-43.02 ^a	-44.94	1.92	1-Ethylcyclopentene	-5.8 ^a	-11.7	5.9
<i>trans</i> -1,3-Dimethylcyclohexane	-42.20 ^a	-44.94	2.74	Methylenecyclopentane	2.4 ^a	-3.9	6.3
<i>cis</i> -1,4-Dimethylcyclohexane	-42.22 ^a	-44.94	2.72	Ethylidenecyclopentane	-4.5 ^a	-11.7	7.2
Ethylcyclohexane	-41.05 ^a	-42.99	1.94	Cyclopentadiene	32.24 ^a	29.3	2.9
Propylcyclohexane	-46.20 ⁱ	-48.12	1.92	Cyclohexene	-0.84 ^a	-3.3	2.5
Cycloheptane	-28.34 ^a	-35.91	7.57	1-Methylcyclohexene	-10.0 ^a	-11.7	1.7
Cyclooctane	(-29.7 ^a	-41.04	11.7	1-Ethylcyclohexene	-15.0 ^a	-16.8	1.8
	(-30.06 ^c		9.98	Methylenecyclohexane	-7.2 ^a	-9.1	1.9
Cyclononane	-31.8 ^a	-46.17	14.4	Ethylidenecyclohexane	-13.7 ^a	-16.8	3.1
Cyclodecane	-36.29 ^a	-51.30	15.01	1,3-Cyclohexadiene	26.0 ^a	24.1	1.9
				1,4-Cyclohexadiene	26.3 ^a	24.1	2.2
				Cycloheptene	-1.8 ^a	-8.5	6.7
				1-Methylcycloheptene	-10.5 ^a	-16.8	6.3
				Methylenecycloheptane	-8.2 ^a	-14.2	6.0
				1,3-Cycloheptadiene	22.9 ^a	19.0	3.9
				1,3,5-Cycloheptatriene	44.5 ^a	46.5	-2.0
				<i>cis</i> -Cyclooctene	-6.2 ^a	-13.6	7.4
				<i>trans</i> -Cyclooctene	3.1 ^a	-13.6	16.7
				1,3,5-Cyclooctatriene	43.7 ^a	41.3	2.4
				Cyclooctatetraene	71.3 ^a	68.8	2.5
				<i>cis</i> -Cyclononene	-7.2 ^a	-18.7	11.5
				<i>trans</i> -Cyclononene	-4.3 ^a	-18.7	14.4
				Norbornene	24.7 ^b	-2.5	27.2
				Norbornadiene	59.7 ^b	+25.0	34.7
Polycycloalkanes ^b							
Bicyclo[1.1.0]butane	51.9 ^a	-14.58	66.5				
1,3-Dimethylbicyclo[1.1.0]butane	39.3 ^a	-30.96	70.0				
Spiropentane	44.23 ^a	-20.82	65.05				
Bicyclo[2.1.0]pentane	37.6 ^a	-19.71	57.3				
Bicyclopropyl	31.0 ^d	-24.84	55.8				
Bicyclo[3.1.0]hexane	9.07 ^a	-24.84	33.91				
1,3,5-Trimethylbicyclo[3.1.0]-hexane	-15.5 ^f	-46.08	30.6				
Bicyclo[4.1.0]heptane	0.32 ^a	-29.97	30.29				
Bicyclo[2.2.1]heptane	-12.42 ^e	-29.97	17.55				
Cubane	148.7 ^b	-17.28	166.0				
Bicyclo[5.1.0]octane	-3.87 ^a	-35.10	31.23				
Bicyclo[2.2.2]octane	-24.09 ^a	-35.10	11.01				
<i>cis</i> -Bicyclo[3.3.0]octane	-22.3 ^c	-35.10	12.8				
<i>trans</i> -Bicyclo[3.3.0]octane	-16.3 ^c	-35.10	18.8				
<i>cis</i> -Bicyclo[4.2.0]octane ^j	-6.1	-35.10	29.0				
Bicyclo[6.1.0]nonane	-7.42 ^a	-40.23	32.81				
<i>cis</i> -Bicyclo[4.3.0]nonane	-30.41 ^c	-40.23	9.82				
<i>trans</i> -Bicyclo[4.3.0]nonane	-31.45 ^c	-40.23	8.78				
<i>cis</i> -Decalin	-40.45 ^c	-45.36	4.91				
<i>cis</i> -Bicyclo[5.3.0]decane ^j	-31.1	-45.36	14.3				
<i>trans</i> -Bicyclo[5.3.0]decane ^j	-31.4	-45.36	14.0				
Nortricyclene	23.8 ^b	-24.03	47.0				
Quadricyclene	83.6 ^b	-18.09	101.1				
Hexacyclo[5.4.1.0 ^{2,6} .0 ^{3,10} .0 ^{6,9} .0 ^{8,11}]dodecane ^k	24.0 ^f	-31.89	55.9				
<i>trans-anti-trans</i> -Perhydroanthracene	-52.74 ⁱ	-59.94	7.70				

^a Taken from the summary in ref 20. ^b R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Amer. Chem. Soc.*, **90**, 4315 (1968); K. B. Wiberg and R. A. Fenoglio, *ibid.*, **90**, 3395 (1968). ^c Taken from the summary in ref 14. ^d A. E. Beezer, W. Lüttke, A. de Meijere, and C. T. Mortimer, *J. Chem. Soc., B*, 648 (1966). ^e Data from Table V. ^f C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962, p 45. ^g The ΔH_f° calcd values for these compounds were calculated by using the olefinic increments of Benson²⁰ in conjunction with our own single conformation alkane increments. ^h See also Table IV. ⁱ Reference 21. ^j Reference 27; R. H. Boyd, private communication. ^k Corrected nomenclature.

whereas the average CC bond length in the *n*-alkanes⁴¹ is 1.533 Å. Allinger's calculations are aimed at reproducing microwave bond lengths, which are somewhat shorter than diffraction values.^{14,42} The 1.526-Å CC

length in propane⁹ and other alkanes is well accounted for by the calculations, but the CC bond lengths for adamantane, norbornane, and bicyclo[2.2.2]octane are generally shorter than the propane value: 1.521, 1.513–1.526, and 1.522–1.529 Å, respectively, contrary

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(42) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1961).

Table VIII. Application of Various Nonbonded Potentials to Adamantane^a

	$d_{\min}(\text{CC})^b$ Å	Calcd <i>anti</i> - butane ^c energy	ΔE_{CC}^d (<i>gauche</i>)	ΔSE^d (<i>gauche</i>)	Calcd adamantane energy	ΔE_{CC}^e (A-D)	ΔSE^e (A-D)
Abe, Jernigan, and Flory ^f	3.60	-1.80	0.31	0.38	2.88	4.62	6.38
Allinger, <i>et al.</i> ^g	3.32	-0.87	-0.01	0.80	-0.54	0.20	2.69
Bartell ^h	3.50	0.22	0.09	0.60	3.59	1.90	2.84
Bartell (CH hard) ^h	3.50	0.70	0.09	0.57	5.08	1.82	2.60
Bartell (CC hard) ^h	3.60	0.21	0.20	0.72	6.50	3.26	4.51
Borisova and Vol'kenshtein ^h	3.73	-1.57	0.27	0.25	0.91	3.25	4.85
Hendrickson ⁱ	3.51	0.75	0.06	0.54	3.25	0.92	1.86
Kitaygorodsky ^j	3.77	-1.87	0.31	0.48	0.93	4.00	5.84
McCullough and McMahon ^k	3.40	1.91	-0.03	0.59	7.04	1.18	2.64
Pauncz and Ginsburg ^l		15.54	0.00	1.57	42.48	0.00	-0.80
Scott and Scheraga ^m	3.20	1.22	-0.08	0.48	2.41	0.09	1.05

^a Energies computed as per ref 3; force constants from ref 37; torsional functions taken from the same papers as nonbonded functions. If no torsional function was given in the references cited, one giving a 3.0-kcal barrier in ethane was used. All energies in kilocalories per mole. ^b Van der Waals minimum in C...C interaction function. ^c Calculated energy of transoid *n*-butane. ^d Change in C...C interaction energy (ΔE_{CC}) and strain (ΔSE) on going from *anti* to *gauche* *n*-butane. ^e Adamantane-*trans*-decalin C...C interaction energy (ΔE_{CC}) and strain energy (ΔSE) differences. ^f A. Abe, R. L. Jernigan, and P. J. Flory, *J. Amer. Chem. Soc.*, **88**, 631 (1966). ^g Bartell³⁸ functions, modified by displacement of indicated function (see text). ^h Equations 4, 6, 7 of N. P. Borisova and M. V. Vol'kenshtein, *J. Struct. Chem. USSR (Eng. Transl.)*, **2**, 324 (1961). ⁱ J. B. Hendrickson, *J. Amer. Chem. Soc.*, **89**, 7036, 7043, 7047 (1967). ^j A. I. Kitaygorodsky, *Tetrahedron*, **14**, 230 (1961). ^k R. L. McCullough and P. E. McMahon, *Trans. Faraday Soc.*, **60**, 2089 (1964). ^l R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960). No C...C function was used by these workers. ^m R. A. Scott and H. A. Scheraga, *J. Chem. Phys.*, **42**, 2209 (1965). ⁿ Reference 14. ^o Reference 38.

to experiment. The underweighting of C...C nonbonded repulsions is apparently responsible for this defect.³

From Table VIII it is clear that the unmodified nonbonded interaction functions of Bartell³⁸ are inadequate for calculating the adamantane-*trans*-decalin strain difference (4.7 kcal from Table IV, strain-free increments). Even the skew-interaction energy of 0.7 kcal from the skew-separate derivation above is somewhat underestimated. Making the C...H function harder by displacing it 0.07 Å along the R_{CH} axis away from the origin has, as expected, little effect. But by hardening the C...C function by displacing it 0.10 Å (using the unmodified CH function), the adamantane-*trans*-decalin strain difference is increased to 4.5 kcal/mol, and even the absolute energies are reasonable (the energy for cyclohexane is calculated to be 1.24 kcal/mol in this force field). Inspection of Table VIII shows that only for those functions having a C...C van der Waals minimum at 3.60 Å or greater will the adamantane-*trans*-decalin difference be of reasonable magnitude.³

A rationalization of the strain in adamantane is thus quantitatively possible using the methods of conventional conformational analysis. The analysis further indicates that C...C repulsions of the type found in all chair-form cyclohexane rings are primarily responsible for the adamantane strain. In cyclohexane, these C...C repulsions are relieved by bond-angle and torsional-angle deformations; in adamantane as in other cage molecules only CC bond stretching affords relief. Force fields that underweight CC repulsions are therefore expected to reproduce the energies of these molecules poorly and give overly short CC bond lengths.

Zero-Point Energy Corrections. There is one further possible origin for the discrepancy between the experimental heat of formation of adamantane and that given by group increments. In deriving the increments the tacit assumption is made that zero-point energies obey group additivity rules and are unaffected by strain.

There has been little work to date bearing on these points. Zero-point energy differences are known to contribute heavily to acyclic hydrocarbon isomerization energies,¹⁹ and this fact was recognized by Bartell⁴³

in his calculation of acyclic hydrocarbon strains, though other workers in conformational analysis have tended to ignore it. The success of the group-increments method for acyclic hydrocarbons is evidence that a group-additivity relation for zero-point energies also exists. Indeed, Pitzer and Catalano⁴⁴ found a zero-point energy increment of 17.70 kcal/mol per CH₂ group for the *n*-alkanes propane through *n*-pentane. Allen³² found that irregularities in his bond-energy additivity scheme were not affected by making corrections to 0°K and removing zero-point energies.

In the case of adamantane, the assumption of group additivity for zero-point energies can be checked. Though all of the fundamental frequencies for adamantane have not been observed, Snyder and Schachtschneider³⁷ have reported their calculated frequencies for adamantane in their vibrational analyses of the saturated hydrocarbons. From these frequencies, and those computed for cyclohexane and *trans*-decalin, the following zero-point energies can be computed: cyclohexane, 103.36 kcal/mol, *trans*-decalin, 160.59 kcal/mol, and adamantane, 148.58 kcal/mol. From cyclohexane a CH₂ increment of 17.23 kcal/mol can be computed. This value is only in fair agreement with the value of Pitzer and Catalano.⁴⁴ The fault may lie in inaccuracies in their data, which came from several sources, or in the calculated frequencies of Snyder and Schachtschneider.³⁷ Using the CH₂ increment from cyclohexane, a CH increment of 11.39 kcal/mol is obtained from *trans*-decalin. These increments give an adamantane zero-point energy of 148.91 kcal/mol, in good agreement with the value obtained from the calculated frequencies, 148.58 kcal/mol. We thus conclude that zero-point energy contributes little—perhaps 0.33 kcal/mol—to the adamantane strain.

Conclusions

1. Existing schemes for the calculation of heats of formation and atomization of alkanes often give poor

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results when applied to cycloalkanes free of the type of skew interactions found in acyclic alkanes. The Tatevskii, Laidler, and Franklin schemes are conspicuously bad in this respect and should not be used for estimating the strain in adamantane. In conformational analysis terminology, the failure of such schemes is due to the lack of corrections for varying numbers of skew conformations present in different systems.

2. Schemes which correct for the number of skew interactions give excellent results for both acyclic and cyclic molecules. From a somewhat more sophisticated point of view, though, strain should be defined using schemes which have been corrected for the existence of skew-containing conformers present at equilibrium in the strain-free acyclic alkanes. We call our scheme a single-conformation one.

3. Using such single-conformation increments, as strain free as possible, adamantane is found to be appreciably strained—6.48 kcal/mol—relative to acyclic alkanes in *gauche*-free staggered conformations. Similarly, cyclohexane (1.35 kcal/mol) and *trans*-decalin (1.79 kcal/mol) possess modest strain energies.

4. The strain energy in adamantane is explicable in

terms of angle strain and nonbonded interactions—predominantly C···C repulsions. These C···C repulsions are unexceptional and are common to all structures containing cyclohexane rings in chair conformations. In *trans*-decalin and larger molecules consisting of fused cyclohexanes, attractive C···C interactions are significant and even reduce the strain on a “per ring” basis. This is not so for polycyclic cage structures, *e.g.*, adamantane.

5. The strain in adamantane can be accounted for quantitatively once the C···C underweighting present in most sets of nonbonded potentials derived from properties whose values are fixed predominantly by H···H interactions is recognized and corrected.

6. The introduction of “cage” or other special effects to explain data for adamantane and other polycyclic molecules is not warranted at this time.

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Carbon-13 Magnetic Resonance. XV.¹ Nonalternant Hydrocarbons

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Abstract: Carbon-13 chemical shifts have been determined for the nonalternant hydrocarbons, azulene, acenaphthylene, fluoranthene, and benzo[*ghi*]fluoranthene. In addition supporting data on acenaphthene and 1,8-dimethylnaphthalene are presented. Spectral assignments were made using selective decoupling techniques and nuclear Overhauser effects. The large chemical-shift range observed in the nonalternant systems (14–22 ppm) compared to the alternant systems (<10 ppm) is considered to provide a marked distinction between these categories of compounds. A discussion of the factors contributing to these shifts including both π - and σ -electronic contributions, obtained using the CNDO/2 method, is presented. It is emphasized that the chemical shifts are not simply related to π -electron charge but that both π - and σ -electronic variations must be considered for the majority of alternant and nonalternant hydrocarbons.

The value of the carbon-13 chemical shifts in providing an insight into the electronic structure of aromatic compounds has been clearly indicated.^{3–11}

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Lauterbur,³ Spiesscke and Schneider,⁴ LaLancette and Benson,⁵ and Lippmaa and coworkers⁶ have shown that carbon-13 shifts vary by approximately 160–200 ppm per unit of π -electron charge in substituted benzenes,³ nonalternant hydrocarbons,³ in the series C₅H₅[−], C₆H₆, C₇H₇⁺,⁴ and C₉H₉[−],⁵ and in the mesitylenonium ion.⁶ Similar charge dependence has been observed in nitrogen heteroaromatic systems^{7–11} provided σ -polarization terms are also considered.

Theoretical considerations^{7–12} have provided some justification for the chemical-shift dependence on π -electron density, though a dependence on mobile bond orders^{8,12} and σ -electronic variations^{8–11} has also been stressed. However, a note of caution has very recently been added.¹³ In the isoelectronic series

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