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Formal Steric Enthalpy[1]

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In the present study we describe a new quantitative measure of steric effects, formal steric enthalpy. FSE provides for the first time the transferability of results of molecular mechanics computations or of other computations of steric properties. Steric energies as calculated by molecular mechanics are force-field dependent and cannot even in principle serve as unbiased measures of steric effects. Moreover, steric energies are highly sensitive to even minor variations in the force field and in the details of its application. As a consequence steric energies reported from one laboratory cannot usually be reproduced reliably in other laboratories. Formal steric enthalpy, on the other hand, is a rigorously defined, though initially unknown, property of a given conformer. It is an unbiased and transferable measure of steric properties independent of method of estimation. If two or more force fields lead to different FSE values for some specific net of conformers, then some or all of the force fields are not adequately calibrated. FSE's provide for the first time the possibility of developing definitive tables of steric properties in much the same way that pK_a's provide definitive tables of acidity. In particular, FSE values are suitable for pairwise comparisons of steric properties of any two molecules; pairwise comparisons of steric energies are limited to isostructural molecules such as members of a family of conformers.

The enthalpy of formation of a molecule in a given medium may conceptually be partitioned into four components, bonding, polar, steric, and medium. These may be designated as formal bonding enthalpy, FBE, formal steric enthalpy, FSE, formal polar enthalpy, FPE, and formal medium (or solvent) enthalpy, FME: eq 1.[6-8] The dissection is a formal one since the criteria for doing so must be selected arbitrarily; the validity of the dissection rests upon the successes it achieves in practice.

$$\Delta H_f = \text{FBE} + \text{FSE} + \text{FPE} + \text{FME} \qquad (1)$$

A well-known application of eq 1 is the expression of the enthalpy of formation of gaseous alkanes as a summation of group increments (principally a FBE term) plus a steric correction (principally at FSE term), eq 2.[9-14] The success of this partitioning shows that bonding enthalpy increments may in a favorable circumstances be treated as localized:[14] That is, the increment of bonding enthalpy for, say, a CH_2 group in RCH_2R' is relatively independent of R and R′ providing that R and R′ are alkyl groups. Although eq 2 reproduces ΔH_f values rather accurately, the separate FBE and FSE components have not proved useful, primarily because the definitions implied are rather crude.

$$\Delta H_f = b(CH_3)n(CH_3) + b(CH_2)n(CH_2) + b(CH)n(CH) + \mathrm{b}(C)n(C) + \text{steric terms} \qquad (2)$$

Since polar effects are small in alkanes, it is reasonable to assign a value of zero to the FPE term for any alkane; alternative assumptions lead to complications that are difficult to manage. In the gas phase the FME term is also defined to be zero. In the following we will consider only the FBE and FSE terms, assigning zero to the FPE and FME terms throughout.

Another useful partitioning represents the ΔH_f for the single conformer of lowest energy by some variant of eq 3.[2,3,5,15,16] The several terms are as follows: ΔH_f(compd)

$$\Delta H_f(\text{compd}) - \text{SM} = \text{base(HF)} + \text{SE} = \Delta H_f(\text{single conformer}) \qquad (3)$$

is the enthalpy of formation of the gaseous alkane, which is usually a mixture of conformers; SM is a statistical mechanical term which serves to correct the observed ΔH_f of the mixture to the ΔH_f of the single conformer of lowest energy; SE is the steric energy computed by molecular mechanics for this coformer. Base(HF) is a summation of group increments, eq 4, the *c* values having been derived

$$\text{base(HF)} = a(CH_3)n(CH_3) + a(CH_2)n(CH_2) + a(CH)n(CH) + a(C)n(C) \qquad (4)$$

so that eq 3 and 4 reproduce the ΔH_f values of a selected set of alkanes. The ΔH_f for the single conformer includes all vibrational, rotational, and librational components appropriate to the assumed temperature (usually 298 K).

Equations 3 and 4 reproduce enthalpies of formation very closely for the sets of alkanes examined, but they do not provide an adequate separation of FBE and FSE. The difficulty lies in the circumstances that steric energies are force-field dependent; they consist of the desired FSE plus a variable residual of FBE, which may be either positive or negative. Examples of these limitations are presented below in the Discussion.

We therefore abandon these definitions of FBE and FSE as being inadequate. We seek instead a more precise general method for separating the FBE and FSE terms for alkanes. The fundamental postulate may be stated explicitly: the FBE term for any alkane may be derived usefully as a strictly additive property based on a counting

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(1) SE, steric energy as calculated by molecular mechanics; FSE, formal steric enthalpy as defined in the present study; ALL71 the Allinger 1971 force field;[2] DETSB, the DeTar–Binzet force field developed in the present study; SCH73, the Schleyer 1973 force field;[3] WHI77, the White 1977 force field;[4] MM2, the Allinger 1977 force field.[5]

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of structural units. The FBE term is to be defined as that calculated for the corresponding "strain-free" molecule having the same constitutive units. We will derive appropriate values of the required FBE increments from enthalpies of formation or from steric energies of suitable sets of molecules which we define to be "strainless" or for which we assign suitable FSE values.

There are two principal meanings for the term "strain energy" and they tend to be applied interchangeably although they are distinct. One is "total strain energy",[17] which is a property of a population of conformers. The other is single-conformer strain energy, a property suggested originally by Schleyer[15] but not actually calculated by him; what he reported were estimates of "total strain energy". Allinger refers to single-conformer strain energy as "inherent strain".[17]

We now show how the concept of single-conformer strain energy may be modified and extended to yield a more precise and a more general quantity, the formal steric enthalpy. We consider first the underlying principles.

The bond energy of a given C unit depends on what other atoms are directly attached; different increments are needed to represent the bond energy due to different combinations of C–C and C–H bonds as in the CH_3, CH_2, CH, and C units. In a sequence of atoms such as C–C–C the bond energy of the central C unit will also depend on the C–C–C angle; the hybridization about the central carbon atom is a function of bond angles (geometry) or more precisely of valence angles (a bonding concept).[18] The C–C–C angle may be less than 90° or it may be more than 130° in what is nominally a sp^3 environment. Strictly speaking, therefore, the bond energy of a C unit is not independent of environment. We may, nevertheless, adopt the common practice of defining steric effects conceptually as being the energy arising from deformations of bonds, angles, and torsions together with the energy due to intramolecular nonbonded interactions. Thus we assign to the formal steric enthalpy term not only nonbonded repulsions and attractions but also all the attendant changes in bonding energy consequent on alterations of the geometry.

The formal bond enthalpy term of eq 1 is the enthalpy of formation of a hypothetical "strain-free" molecule composed of the designated structural units. The formal steric enthalpy of a given conformer is defined operationally as the difference between the enthalpy of formation of that single conformer and the formal bond enthalpy for formation of the molecule, eq 1 with FPE and FME both zero.

We turn next to a point of some controversy, viz, the significance of steric energies. In a recent very careful study there appears the statement "EFF results refer to isolated molecules in a hypothetical, motionless state at 0 K."[19] EFF (empirical force field) results are the quantities that we refer to as steric energies. This statement is incorrect. It perhaps arises from the circumstance that a molecular mechanics calculation is necessarily carried out on a static arrangement of atoms defining one single conformation. However, the way a calculation is performed has no necessary bearing on its theoretical significance.

What has been overlooked in the quoted statement is the origin of the constants used in the force field. As shown in eq 3, the constants of the force field and the group increments have both been selected so as to reproduce enthalpies of formation at some designated temperature, usually 25 °C; they do not reproduce the energy of a molecule at 0 K. SE's pertain to the conditions appropriate to the data used in the calibration of the force field, most commonly real molecules, gas phase, usually 298 K. Molecular mechanics does not give absolute energies; it serves rather as a powerful tool for interpolating and extrapolating structural and thermodynamic data. There is no reason in principle why a force field could not be calibrated to reproduce the energies of vibrationless molecules at 0 K, but the commonly used force fields have not been so calibrated.

Steric energies based on any of the published force fields must, therefore, include zero point vibrational components and heat capacity components. They pertain to the enthalpy of formation of some specific conformer at a temperature remote from absolute zero. To compare calculated energies with experimental energies of real gases it is, of course, necessary to correct for the presence of multiple conformers as is the purpose of the SM term of eq 3.

Whereas past definitions of "strain energies" have been tied to observed enthalpies of formation, the above definition explicitly removes this restriction. It is possible to develop sets of group increments for any given force field that will remove the residual bond enthalpy component and make it possible to calculate the formal steric enthalpy whether or not the experimental enthalpy of formation has been measured.

In the next section we develop detailed procedures for defining and calculating formal steric enthalpies. Providing these definitions have been developed for some given class of molecules, the only steps required to calculate appropriate corrections are to get the steric energies for the designated standard conformers.

Formal steric enthalpies are theoretically a transferable measure of steric properties; they are practically transferable since all requisite calculations, specifically including those of the standards, are to be carried out in one laboratory using a rigorously applied protocol. This means that one single force field is to be used throughout for the entire set of molecules under consideration and that it is to be applied uniformly to the entire set, including the defining standards. Although raw steric energies may vary somewhat erratically by many tenths of a kilocalorie for even rather minor variants of a given force field, the derived parallel series of formal steric enthalpies for calculations based on minor variants of nominally the same force field may be expected to be closely similar. We illustrate this important characteristic below.

Definition of Formal Steric Enthalpies of Alkanes. The general procedure for defining FSE's for some given class of molecules involves three steps: identification of a minimum set of structural units necessary for describing any member of the set, selection of suitable standard molecules containing these units, and assignment of reasonable values of FSE's to appropriate conformers of the molecules of the standard set. By this latter step we define formally and precisely what we mean by "strain-free" molecules. For alkanes eq 5 and 6 show the relationship

$$\mathrm{FSE} = \mathrm{SE} - \mathrm{base(ffcorr)} \tag{5}$$

$$\mathrm{base(ffcorr)} = d(\mathrm{CH_3})n(\mathrm{CH_3}) + d(\mathrm{CH_2})n(\mathrm{CH_2}) + d(\mathrm{CH})n(\mathrm{CH}) + d(\mathrm{C})n(\mathrm{C}) \tag{6}$$

between the calculated steric energy (SE) and the formal steric enthalpy (FSE). The correction terms, the d values of eq 6, are to be derived from the calculated SE's and the defined FSE's of the chosen set of standard conformers.

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Table I. Group Increments

force field	*c*(CH3)[a]	*c*(CH2)	*c*(CH)	*c*(C)	*d*(CH3)[b]	*d*(CH2)	*d*(CH)	*d*(C)
SCH73[c]	-10.671	-5.717	-2.912	-.770	0.598	0.580	0.709	0.628
SCH73[d]	-10.671	-5.647	-2.980	-.892	0.598	0.580	1.109	1.428
ALL71[c]	-11.315	-5.752	-.632	4.936	1.242	0.615	-1.571	-5.078
ALL71[d]	-11.315	-5.682	-.700	4.814	1.242	0.615	-1.171	-4.278
WHI77[c]	-10.322	-5.246	-2.391	-.791	0.249	0.109	0.188	0.649
WHI77[d]	-10.322	-5.176	-2.459	-.913	0.249	0.109	0.588	1.449
DETSB[c]	-10.194	-5.922	-4.440	-4.945	0.121	0.785	2.237	4.803
DETSB[d]	-10.194	-5.852	-4.508	-5.067	0.121	0.785	2.637	5.603
EXP H_f[c]	-10.073	-5.137	-2.203	-.142				
EXP H_f[d]	-10.073	-5.067	-1.871	0.536				

[a] Equation 8. [b] Equation 6. [c] Based on FSE = 0.7 for isoalkanes and FSE = 1.4 for neoalkanes and SM calculated using 0.7 for each gauche interaction and 1.25 for each g^+g^- sequence. [d] Based instead on FSE = 0.3 for isoalkanes and 0.6 for neoalkanes SM calculated using 0.3 for each gauche interaction and 1.25 for each g^+g^- sequence.

At the request of a referee we illustrate these calculations in the Appendix.

"Experimental" FSE values are defined implicitly by eq 7 and 8. The experimental FSE is the FSE of the conformer of lowest energy; it is the difference between the experimental single conformer ΔH_f, obtained by subtracting the SM correction from the observed ΔH_f (eq 3), and the formal bond enthalpy estimated by eq 8.

$$\Delta H_f(\text{single conformer}) = \text{FBE} + \text{FSE} \qquad (7)$$

$$\text{FBE} = c(\text{CH}_3)n(\text{CH}_3) + c(\text{CH}_2)n(\text{CH}_2) + c(\text{CH})n(\text{CH}) + c(\text{C})n(\text{C}) \qquad (8)$$

$$a(\text{x}) = c(\text{x}) - d(\text{x}) \qquad (9)$$

The FBE group increments, the *c* values of eq 8, are to be based on the same set of conformers of standard molecules used for calculating the *d* values of eq 6. The *a* values for a given force field are derived from the experimental single-conformer ΔH_f values together with the assigned FSE's for the conformers of lowest energy of the molecules of the standard set, eq 7. The *a* values of eq 4 may be derived from the *c* values and the *d* values by use of eq 9. The *a* values or their equivalents have been reported previously in the derivation of calculated ΔH_f values, that is ΔH_f(compd), eq 3.[2,3,5,15,16]

The FSE's defined by eq 7 are single-conformer strain energies; these are "inherent strain" values in Allinger's terminology.[17] The derivation of suitable SM values is described below. Formal steric enthalpies are more general than are "strain energies"; FSE values may be defined and calculated whether or not enthalpies of formation are available and whether or not the molecules are stable.

For alkanes it has generally been found adequate to use four structural units to represent bond energies as in eq 2 and 4. These are CH_3, CH_2, CH, and C. We will use these same units for eq 6 and 8. If methane is to be included, then a special (and hence trivial) methane increment must be added. It is necessary to be aware that other special cases may necessitate additional structural units. Cyclopropanes may, for example, require adoption of a separate cyclopropyl group increment. The reason is not based primarily on problems of deriving an angle function that will accommodate a three-membered ring. It is based on the premise that bonding in three-membered rings is qualitatively different from bonding in acyclic alkanes or in cycloalkanes with no ring smaller than four carbon atoms. The present treatment is based on just the four alkyl units.

A critical step in establishing FSE's for a given class of molecules is the selection of appropriate standard molecules and assignment of suitable values of the FSE's to specified conformers of these standard molecules. Once questions of standards have been settled, derivation of the correction terms *d* and the single conformer increments *c* becomes a routine matter.

The selection of standards for alkanes is particularly critical since alkanes provide the values for the widely occurring alkyl units. Our preference is to avoid ethane, propane, isobutane, and neopentane since as initial members of the series their ΔH_f's are exceptional.[9,11] The SE values of these initial alkanes may likewise be exceptional.

In principle we need just four standards to determine *d*, *a*, and *c* values for four structural units. There are, however, advantages to using a larger number of standards, particularly with alkanes, in order to obtain the best possible average values of increments.

We base the correction terms for CH_3 and for CH_2 on the five alkanes from butane through octane, adopting the common practice of defining the FSE's to be 0 for the all s-trans conformers. The correction terms *d* and the group increments *a* and *c* may be derived either by a simple least-squares procedure or by averaging.

We derive the correction terms for CH from the isoalkanes from 2-methylbutane through 2-methyloctane with FSE assigned to be 0.7 kcal/mol, and we derive separately the correction term for C from the neoalkanes from 2,2-dimethylbutane through 2,2-dimethylhexane with FSE 1.4. The defined FSE's are for the conformers of lowest steric energy.

Since SE and ΔH_f values are less certain for isoalkanes and for neoalkanes than for *n*-alkanes, the preferable statistical procedure is to perform the calculations as indicated rather than to obtain all values in a single multiple regression. An "overall" method would tend to corrupt the correction terms for the CH_3 and the CH_2 groups without improving the values for the CH and the C groups.

An important consideration in choosing these proposed standards for the alkanes is that enthalpies of formation are available for all of them. It therefore becomes possible to make a consistent comparison of FSE's based on "experiment" with FSE's based on calculation. This consideration cannot be universally adopted for other types of molecules owing to lack of the necessary thermodynamic data.

The above assignments of standards results in the correction terms *d* and the group increments *c* listed in Table I. The *a* terms are obtainable by use of eq 9. Comparison with previous work shows that the *c* values (eq 4) are comparable with published values, as they should be.[2,3,5,15,16] The *d* values are new.

In the Discussion we take up the question of choosing alternative values of FSE for the standards, the values of 0.3 for isoalkanes and 0.6 for neoalkanes. The respective correction terms for this choice are also given in Table I.

Formal Steric Enthalpies of Alkanes Based on Four Different Force Fields. We now demonstrate the use of FSE values in the comparison of four representative

Table IIA. Formal Steric Enthalpies (0.7, 1.4 Set)

alkane	$-\Delta H_f$[a] 298	SD[b] ΔH_f	SM[c]	exptl[d] FSE	gauche[e] enthalpy	Δ (exptl − gauche)[f]	ALL71[g] SE	ALL71[h] FSE	SCH73[i] SE	SCH73[h] FSE	WHI77[j] SE	WHI77[h] FSE	DETSB[k] SE	DETSB[h] FSE
ethane	20.24	0.12	0.00	−0.08	0.00	−0.08	2.37	−0.11	1.04	−0.16	0.27	−0.23	0.25	0.01
propane	24.82	0.14	0.00	0.46	0.00	0.46	3.08	−0.02	1.72	−0.06	0.54	−0.07	1.02	−0.01
butane	30.15	0.16	0.27	0.00	0.00	0.00	3.71	0.00	2.35	−0.01	0.71	−0.01	1.81	0.00
pentane	35.00	0.21	0.50	0.06	0.00	0.06	4.33	0.00	2.94	0.00	0.83	0.01	2.60	0.00
hexane	39.96	0.22	0.73	0.00	0.00	0.00	4.95	0.01	3.52	0.00	0.94	0.01	3.38	0.00
heptane	44.88	0.22	0.96	0.00	0.00	0.00	5.56	0.00	4.10	0.00	1.04	0.00	4.17	0.00
octane	49.82	0.28	1.19	−0.03	0.00	−0.03	6.17	0.00	4.67	−0.01	1.15	0.00	4.95	0.00
2-methylpropane	32.15	0.30	0.00	0.27	0.00	0.27	2.10	−0.06	2.08	−0.42	0.92	−0.02	2.50	−0.10
2-methylbutane	36.92	0.17	0.09	0.55	0.70	−0.15	3.47	0.70	3.80	0.72	1.80	0.76	4.05	0.67
2-methylpentane	41.66	0.24	0.26	0.78	0.70	0.08	4.11	0.73	4.38	0.72	1.86	0.71	4.88	0.71
2-methylhexane	46.59	0.28	0.50	0.74	0.70	0.04	4.69	0.69	4.93	0.69	1.94	0.68	5.67	0.72
2-methylheptane	51.50	0.36	0.73	0.74	0.70	0.04	5.30	0.69	5.50	0.68	2.03	0.66	6.45	0.71
2,4-dimethylpentane	48.28	0.29	0.23	1.33	1.40	−0.07	3.66	1.22	5.66	1.27	2.75	1.27	7.14	1.40
2,5-dimethylhexane	53.21	0.40	0.28	1.48	1.40	0.08	4.69	1.63	6.50	1.53	2.97	1.38	8.09	1.56
2,2-dimethylpropane	39.67	0.24	0.00	0.76	0.00	0.76	−0.38	−0.27	2.16	−0.86	1.57	−0.08	5.06	−0.23
2,2-dimethylbutane	44.35	0.24	0.00	1.22	1.40	−0.18	1.91	1.41	5.03	1.43	3.25	1.50	7.42	1.35
2,2-dimethylpentane	49.27	0.37	0.17	1.27	1.40	−0.13	2.55	1.43	5.59	1.41	3.25	1.39	8.28	1.42
2,2-dimethylhexane	53.71	0.32	0.42	1.72	1.40	0.32	3.10	1.37	6.12	1.36	3.29	1.32	9.07	1.43
3,3-dimethylpentane	48.17	0.00	0.00	2.54	2.80	−0.26					5.24	3.38	10.15	3.29
3,3-dimethylhexane	52.61	0.00	0.17	3.07	2.80	0.27					5.24	3.27	11.04	3.40
2,2,3-trimethylbutane	48.95	0.33	0.00	3.76	2.80	0.96	3.00	3.44	8.68	4.35	5.72	3.64	11.45	3.81
2,2,3-trimethylpentane	52.61	0.37	0.23	5.01	3.50	1.51					6.92	4.73	13.75	5.32
2,2,4-trimethylpentane	53.57	0.37	0.05	4.23	3.35	0.88					5.28	3.09	12.47	4.04
2,3,3-trimethylpentane	51.69	0.38	0.24	5.92	4.20	1.72					8.00	5.81	14.61	6.18
2,2,3,3-tetramethylbutane	53.99	0.49	0.00	6.73	4.20	2.53					9.14	6.35	17.60	7.27
2,2,3,3-tetramethylpentane	56.67	0.42	0.27	8.92	5.60	3.32					11.63	8.73	21.06	9.94
2,2,3,4-tetramethylpentane	56.64	0.36	0.23	8.12	5.45	2.67			13.98	8.35	9.24	6.72	17.91	7.91
2,2,4,4-tetramethylpentane	57.83	0.40	0.00	8.03	5.30	2.73	4.47	6.56	11.68	6.26	8.13	5.23	18.02	6.90
3,3,5,5-tetramethylheptane	66.10	0.80	0.39	9.64	8.10	1.54					11.68	8.56	23.11	10.42
2,2,4,4,5-pentanemethylhexane	67.10	0.80	0.24	10.80	8.10	2.70					12.47	9.13	24.77	11.30
tri-*tert*-butylmethane		0.00					31.67	37.30	48.21	40.24	32.92	28.54	56.26	38.53
std dev, std set plus[l]								0.16		0.16		0.18		0.13
corr coeff sq std set plus[l]								0.935		0.938		0.916		0.959
std. dev, crowded set[m]												1.16		0.60
corr coeff sq. crowded set[m]												0.820		0.951

[a] Reference 11. [b] Reference 9. [c] See text, ref 34. [d] Equations 7–9; *c* and *d* values from Table I. [e] See text. [f] Steric crowding. [g] SE Values calculated by Tenpas;[6] force field ref 2 and Table VI.[20] [h] Equations 5 and 6; *d* values from Table I. FSE values based on standard isoalkanes having FSE of 0.7, neoalkanes 1.4. [i] SE values calculated by Tenpas,[6] force field ref 3 and Table VI.[20] [j] SE values calculated in this study; force field ref 4 and Table VII.[20] [k] SE values calculated in this study; force field of Table VII.[20] [l] Standard set (see text) plus 2,4-dimethylpentane and 2,5-dimethylhexane. [m] The 12 alkanes starting with 3,3-dimethylpentane.

Table III. Formal Steric Enthalpy Differences

		exptl – calcd[a] FSE (0.7 kcal/mol gauche)					exptl – calcd[b] FSE (0.3 kcal/mol gauche)				
alkane	$-\Delta H_f$	exptl FSE	ALL71	SCH73	WHI77	DETSB	exptl FSE	ALL71	SCH73	WHI77	DETSB
ethane	20.24	−0.08	0.02	0.06	0.13	−0.10	−0.08	0.02	0.06	0.13	−0.10
propane	24.82	0.46	0.48	0.51	0.53	0.47	0.39	0.41	0.44	0.46	0.40
butane	30.15	0.00	0.00	0.00	0.00	0.00	−0.02	−0.02	−0.02	−0.02	−0.02
pentane	35.00	0.06	0.05	0.05	0.05	0.05	0.04	0.03	0.03	0.03	0.03
hexane	39.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
heptane	44.88	0.00	−0.01	−0.01	0.00	−0.01	0.00	0.00	0.00	0.00	0.00
octane	49.82	−0.03	−0.03	−0.03	−0.04	−0.04	0.00	0.00	0.00	−0.01	−0.01
2-methylpropane	32.15	0.27	0.32	0.69	0.28	0.37	−0.05	0.39	0.76	0.35	0.44
2-methylbutane	36.92	0.55	−0.15	−0.16	−0.20	−0.11	0.17	−0.13	−0.14	−0.18	−0.09
2-methylpentane	41.66	0.78	0.05	0.05	0.06	0.06	0.34	0.01	0.02	0.03	0.03
2-methylhexane	46.59	0.74	0.05	0.5	0.06	0.02	0.34	0.05	0.05	0.06	0.02
2-methylheptane	51.50	0.74	0.05	0.06	0.08	0.03	0.35	0.06	0.07	0.08	0.03
2,4-dimethylpentane	48.28	1.33	0.10	0.05	0.05	−.07	0.52	0.10	0.05	0.05	−0.07
2,5-dimethylhexane	53.21	1.48	−0.15	−0.04	0.10	−0.08	0.66	−0.17	−0.07	0.07	0.10
2,2-dimethylpropane	39.67	0.76	1.03	1.62	0.83	0.99	0.09	1.15	1.74	0.96	1.11
2,2-dimethylbutane	44.35	1.22	−0.18	−0.20	−0.27	−0.12	0.47	−0.13	−0.15	−0.22	−0.07
2,2-dimethylpentane	49.27	1.27	−0.16	−0.14	−0.11	−0.15	0.41	−0.22	−0.20	−0.17	−0.21
2,2-dimethylhexane	53.71	1.72	0.35	0.35	0.39	0.28	0.92	0.35	0.35	0.39	0.28
3,3-dimethylpentane	48.17	2.54			−0.83	−0.75	1.72			−0.85	−0.77
3,3-dimethylhexane	52.61	3.07			−0.20	−0.33	2.14			−0.33	−0.46
2,2,3-trimethylbutane	48.95	3.76	0.32	−0.59	0.12	−0.04	2.75	0.51	−0.40	0.31	0.14
2,2,3-trimethylpentane	52.61	5.01			0.27	−0.31	3.93			0.39	−0.19
2,2,4-trimethylpentane	53.57	4.23			1.13	0.18	3.14			1.24	0.29
2,3,3-trimethylpentane	51.69	5.92			0.10	−0.26	4.94			0.32	−0.04
2,2,3,3-tetramethylbutane	53.99	6.73			0.38	−0.53	5.38			0.62	−0.29
2,2,3,3-tetramethylpentane	56.67	8.92			0.19	−1.02	7.51			0.38	−0.83
2,2,3,4-tetramethylpentane	56.64	8.12		−0.23	1.39	0.20	6.82		0.07	1.70	0.51
2,2,4,4-tetramethylpentane	57.83	8.03	1.47	1.77	2.80	1.12	6.60	1.64	1.94	2.97	1.30
3,3,5,5-tetramethylheptane	66.10	9.64			1.08	−0.78	8.32			1.35	−0.50
2,2,4,4,5-pentanemethylhexane	67.10	10.80			1.66	−0.50	9.14			2.00	−0.15

[a] Calculated formal steric enthalpies from Table IIA. Differences are also equal to ΔH_f(obsd) – ΔH_f(calcd). [b] Calculated formal steric enthalpies from Table IIB.

force fields. The sets of SE's based on ALL71[2] and on SCH73[3] were available from calculations carried out in or laboratory some years ago.[6,16] The values based on WHI77[4] and on DETSB come from the present study.

These four force fields represent significant contrasts in structure and in parameterization, and accordingly they provide a suitable test as to how close an agreement may be expected for variously computed FSE values. That two of them are no longer current is unimportant for present purposes.

ALL71 is a precursor of MM1 and MM2;[1] it uses stretch–bend interactions and locates the centers for nonbonded interactions to hydrogen about 90% along the C–H bonds. None of the other three force fields uses these features. The nonbonded functions of the early Allinger and Schleyer force fields are considered to be skewed, but in different ways.[4] The White force field was designed to overcome this problem. All three published force fields use the Buckingham exp-6 nonbonded potential function. The DeTar–Binzet force field developed in the present study uses instead the Lennard–Jones 12-6 function.

In Table IIA we present SE and FSE values of a series of acyclic alkanes as computed experimentally and as calculated with the above four force fields. These data are based on the 0.7/1.4 FSE calibration values for isoalkanes and neoalkanes, respectively. In Table IIB (supplementary material)[20] are presented the corresponding results based instead on assignment of 0.30/0.60 values to the standards. The increments needed for both calculations are presented in Table I. As will be shown below, the FSE values in Table IIA are somewhat more consistent than those in Table IIB. We therefore have adopted the 0.7–1.4 values as perferable.

From comments of referees it appears that there is some misunderstanding about the considerable investment in time and in computing resources required to carry out extensive comparisons of force fields even though such comparisons are of great interest. It is not sufficient to perform a series of runs on just the standards since there is no way to be certain that exactly the same set of constants is being used for the standards as in the published calculations. In order to derive FSE values the entire set of calculations must be carried out as a consistent package.

Table III summarizes the differences between "experimental" FSE values and FSE values derived from SE's.

Since FSE values provide a transferable measure of steric effects of conformers, it now becomes possible to undertake to compile definitive tables of FSE values. Table IV is an initial compilation. Such a complication should include a detailed definition of the conformation. It should include both the raw steric energy and the derived FSE values. Should the definitions of the FSE be changed, it might be possible to recompute the new FSE set. For experimental FSE values it is important to include information about the assumed ΔH_f and SM values. We do not know how reliably the calculated FSE values reproduce the "correct" FSE values as defined by the standards. This matter involves questions of the reliability of force fields. It is by comparative computations of FSE values that we can expect to derive improved force fields.

Discussion

Although it is widely appreciated that steric energies cannot properly be compared except among conformers or other isostructural molecules,[17] comments of some referees and implications in some publications[21] suggest

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[20] Supplementary material includes Table IIB, Table IV supplement, Table VI force fields, and pictorial conformational data.

[21] Schneider, H. J.; Schmidt, G.; Thomas, F. *J. Am. Chem. Soc.* **1983**, *105*, 3556.

that the point may not be universally understood. The data of Table IIA provide many illustrations. For example, a comparison of the SE values for hexane and for 2,2-dimethylbutane shows that ALL71 gives 4.95 and 1.91, a decrease of 3 kcal/mol while WHI77 gives 0.94 and 3.25, an increase of 2 kcal/mol. SCH73 and DETSB give further discordant SE comparisons. As a contrast the FSE values are similar for all four force fields; ALL71 gives 0.01 and 1.41 while WHI77 gives 0.01 and 1.50. This exaple illsutrates the transferability of FSE values and the lack of transferability of raw steric energies.

The sensitivity of steric energies to small changes in a force field may be illustrated by the effects of changing the C–H reference distance from 1.100 to 1.113 Å; steric energies for the set of standard conformers decreased by from 0.1 to 0.2 kcal/mol. Although this particular effect is not large, it is an unnecessary perturbation. An accumulation of similar "minor" changes can result in rather large and erratic differences in the steric energies. For the example cited the FSE values were identical with the two force fields to better than 0.01 kcal/mol. A possible problem in using a published force field is the difficulty of being certain that all constants have been correctly identified and correctly applied. To a considerable extent such uncertainties can be obviated if steric energies are converted to formal steric enthalpies. FSE values can be expected to be concordant for closely similar force fields even in the face of minor variations.

We consider next the validity of the FSE values reported in Table IIA and we also consider the performance that can be expected of a force field.

First is the matter of consistency. We consider first the FSE values for the selected conformers of the 12 alkanes chosen as standards plus values for two closely related alkanes, 2,4-dimethylpentane and 2,5-dimethylhexane. One significant test of consistency is the "within alkanes" standard deviation. For the 14 alkanes this is 0.04 kcal/mol; for these not too crowded molecules the four force fields give admirably good agreement. For purposes of comparison the corresponding within alkanes standard deviation of the raw steric energies for these 14 alkanes is 1.95.

Another test of consistency is the comparison of the calculated FSE values with the "experimental" FSE values. For the same set of 14 alkanes (that is, omitting ethane and the propanes) the calculated FSE's agree with the "experimental" FSE's within 0.16 kcal/mol and the squares of the correlation coefficients range from 0.29 to 0.96. These values are summarized at the bottom of Table IIA. On the basis of reported standard deviations the average variance corresponds to an average standard deviation of about 0.3 kcal/mol in the enthalpies of formation. That the variance of the difference between calculated and "experimental" FSE values is smaller than the variance of the experimental data themselves is presumably a result of the smoothing processes used in tabulating the enthalpies of formation.

A third estimate of consistency may be obtained by comparing FSE values with estimates of gauche enthalpies. These are the values in the column labeled "gauche enthalpy"; their derivation is described below. In effect this amounts to comparing the assigned FSE values and the calculated FSE values. For DETSB the standard deviation of this comparison is 0.06 and the square of the correlation coefficient is 0.993. On the basis of these several criteria the FSE values may be judged to be consistently definable.

In Table I we report a set of increments based on alternative FSE assignments of 0.30 kcal/mol for isoalkanes and 0.60 for neoalkanes. The alternative definition leads, of course, to alternative increments for estimating FBE values and to modified though not greatly altered sets of calculated and "experimental" FSE values. The corresponding data for FSE values calibrated on FSE's of 0.3 kcal/mol for isoalkanes and 0.6 kcal/mol for neoalkanes are presented in Table IIB.[20] Although the differences in overall agreement are not large, the values in Table IIA show better accord between calculated and experimental FSE's.

We conclude, therefore, that derivation of consistent and useful estimates of FBE increments is not critically dependent on the FSE values chosen for the standards. Decreasing the standard FSE definition by almost 60% decreases the FSE values of hindered alkanes by perhaps 25%. Although the sensitivity of the calculated FSE values is only moderately dependent on the definitions of the standards, it is clear that the precise FSE values do depend critically on definitions, and it is absolutely essential to work with some one rigidly agreed upon set of standards if the objective is to achieve transferability of FSE values.

Of interest is the closeness of agreement of the FSE values for the more crowded alkanes. For present purposes these are defined as all compounds in Tables IIA and IIB from 3,3-dimethylpentane down. We did not undertake recalculations to fill in missing values for ALL71 and SCH73; there are therefore not enough examples to permit evaluation of the performance of these force fields although a few FSE values for alternative conformers based on ALL71 and SCH73 may be found in Table IV. Parallel data based on WHI77 and DETSB have been calculated in this study for 12 "crowded alkanes". In comparison with the "experimental" FSE's the standard deviation for the WHI77 values is 1.2 kcal/mol and for DETSB values is 0.6; correlation coefficients squared are respectively 0.82 and 0.95. The estimated standard deviation of the enthalpies of formation for these 12 averages to be 0.24 kcal/mol. Uncertainties in some of the SM values may contribute to errors in our estimation of the "experimental" FSE's.

Table IV presents a summary of FSE values for several other conformers of these acyclic alkanes, along with a definition of the conformations. Further conformational detail is available in a more complete version of Table IV in the supplementary material.[20]

It is possible to make limited comparisons with published data. In Table VI of ref 22 values are given for the "inherent strain" of five moderately to highly strained acyclic alkanes. The "inherent strain" values tend to be high in comparison with our experimental FSE values; 9.2 instead of 6.73 for 2,2,3,3-tetramethylbutane, 4.9 instead of 4.2 for 2,2,4-trimethylpentane, and 4.7 instead of 3.8 for 2,2,3-trimethylbutane. The 43.3 kcal/mol value for "inherent strain" of tri-*tert*-butylmethane is considerably higher than any of the four FSE values in Table IIA and some 6 kcal higher than the FSE value obtained with ALL71. These differences arise in part from differences in choice of standard compounds; Allinger uses isobutane and neopentane to derive his strain-free increments for the CH and the C units.[17] No experimental value is available for tri-*tert*-butylmethane.[40]

In their study of tri-*tert*-butylmethane[23] Bartell and Bürgi report the geometry predicted by two force fields.

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(22) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(23) Bartell, L. S.; Bürgi, H. B. *J. Am. Chem. Soc.* **1972**, *94*, 5239.

Table IV. Formal Steric Enthalpies of Conformers of Alkanes[a]

2-methylbutane, C3C6(C9)C14C18
3-6-14-18 171°
t
g
SCH73 3.80 0.72
t
exptl 0.09 0.55 -36.92

2-methylpentane, C3C6(C9)C14C18C22
3-6-14-18 171°, 6-14-18-22 185°
DETSB 4.88 0.71
WHI77 1.86 0.71
SCH73 4.38 0.72
ALL71 4.11 0.73
exptl 0.26 0.78 -41.66

2-methylhexane, C3C6(C9)C14C18C22C26
3-6-14-18 171°, 6-14-18-22 185, 14-18-22-26 180°
DETSB 5.67 0.72
WHI77 1.93 0.68
SCH73 4.93 0.69
ALL71 4.69 0.69
exptl 0.50 0.74 -46.59

2-methylheptane, C3C6(C9)C14C18C22C26C30
3-6-14-18 171°, 6-14-18-22 185°, 14-18-22-26 180°, 18-22-26-30 180°,
3-6-14 111°, 9-6-14 113°, 3-6-9 110°, 14-18-22 113°
DETSB 6.45 0.71
WHI77 2.03 0.66
SCH73 5.50 0.68
ALL71 5.30 0.69
exptl 0.73 0.74 -51.50

2,4-dimethylpentane, C3C6(C9)C14C18(C21)C26
3-6-14-18 184°, 6-14-18-26 184°
DETSB 7.14 1.40
WHI77 2.75 1.27
SCH73 5.66 1.27
ALL71 3.66 1.22
exptl 0.23 1.33 -48.28

2,5-dimethylhexane, C3C6(C9)C14C18C22(C25)C30
3-6-14-18 170°, 6-14-18-22 180°, 14-18-22-30 190°, 9-6-14-18 294°,
14-18-22-25 66°, 6-14-18 115°, 14-18-22 115°
DETSB 8.09 1.56
WHI77 2.97 1.38
SCH73 6.50 1.53
ALL71 4.69 1.63
exptl 0.28 1.48 -53.21

2,2-dimethylbutane, C3C6(C8)(C13)C18C22
3-6-18-22 180°, 3-6-18 108°, 6-18-22 118°
DETSB 7.42 1.35
WHI77 3.25 1.50
SCH73 5.03 1.43
ALL71 1.91 1.41
exptl 0.00 1.22 -44.35

2,2-dimethylpentane, C3C6(C8)(C13)C18C22C26
3-6-18-22 180°, 6-18-22-26 180°, 6-18-22 118°, 18-22-26 113°
DETSB 8.28 1.42
WHI77 3.25 1.49
SCH73 5.59 1.41
ALL71 2.55 1.43
exptl 0.17 1.27 -49.27

2,2-dimethylhexane, C3C6(C8)(C13)C18C22C26C30
3-6-18-22 180°, 6-18-22-26 180°, 18-22-26-30 180°, 6-18-22 118°
DETSB 9.07 1.43
WHI77 3.29 1.32
SCH73 6.12 1.36
ALL71 3.10 1.37
exptl 0.42 1.72 -53.71

3,3-dimethylpentane, C3C6C10(C12)(C17)C22C26
3-6-10-22 180°, 6-10-22-26 180°, 3-6-10 119°, 10-22-26 119°
DETSB 10.15 3.29
WHI77 5.24 3.38
DETSB 11.04 3.40
WHI77 5.24 3.27
exptl 0.00 2.54 -48.17

2,2,3-trimethylbutane, C3C6(C8)(C13)C18(C21)C26
3-6-18-26 185°, 6-18-21 115°, 6-18-26 115°,
8-6-18-26 64°
DETSB 11.45 3.81
WHI77 5.72 3.64
exptl 0.00 3.76 -48.95

2,2,3-trimethylpentane,
C3C6(C8)(C13)C18(C21)C26C30
3-6-18-26 178°, 6-18-26-30 193°, 6-18-26 115°,
18-26-30 116°, 3-6-18-21 307°, 8-6-18-21 189°
DETSB 13.75 5.32
WHI77 6.92 4.73
exptl 0.23 5.01 -52.61

3-6-18-26 188°, 6-18-26-30 205°, 6-18-26 115°,
18-26-30 115°, 3-6-18-21 316°, 8-6-18-21 198°
SCH73 10.92 6.01
ALL71 4.81 4.63
DETSB 13.75 5.32
WHI77 6.92 4.73

3-6-14-26 174°, 6-14-26-30 187°, 3-6-14 116°,
9-6-14 115°, 9-6-14-26 303°, 3-6-14-16 295°
DETSB 14.61 6.18
WHI77 8.00 5.81

2,2,4-trimethylpentane,
C3C6(C8)(C13)C18C22C(C25)C30
3-6-18-22 185°, 6-18-22-30 217°, 13-6-18 112°,
6-18-22 120°, 18-22-25 113°, 8-6-18-22 66°
DETSB 12.47 4.04
WHI77 5.28 3.09
exptl 0.05 4.23 -53.57

3-6-18-22 163°, 6-18-22-30 187°, 13-6-18 112°,
6-18-22 123°, 18-22-25 115°, 8-6-18-22 44°
DETSB 12.68 4.25
SCH73 8.91 4.00
ALL71 4.20 4.02
WHI77 5.62 3.43

2,2,3,3-tetramethylbutane,
C3C6(C8)(C13)C18(C20)(C25)C30
3-6-18-30 180°, 3-6-18-20 300°, 3-6-18-25 60°,
8-6-18-30 60°
DETSB 17.60 7.27
WHI77 9.14 6.35
exptl 0.00 6.73 -53.99

3-6-18-30 197°, 3-6-18-20 317°, 3-6-18-25 77°,
8-6-18-30 77°
ALL71 3.08 5.78
SCH73 12.41 7.57

2,2,3,3-tetramethylpentane,
C3C6(C8)(C13)C18(C20)(C25)C30C34
3-6-18-30 190°, 6-18-30-34 187°, 3-6-18-20 311°,
3-6-18-25 69°, 8-6-18-30 71°, 13-6-18-30 310°
DETSB 21.06 9.94
WHI77 11.63 8.84
exptl 0.27 8.92 -56.67

3-6-18-30 198°, 6-18-30-34 299°, 3-6-18-20 317°,
3-6-18-25 74°, 8-6-18-30 79°, 13-6-18-30 317°
DETSB 22.28 11.16

2,2,3,4-tetramethylpentane,
C3C6(C8)(C13)C18(C21)C26(C29)C34
3-6-18-26 182°, 6-18-26-34 219°, 6-18-26-29 92°,
21-18-26-34 84°, 6-18-21 115°, 6-18-26 117°
WHI77 9.24 6.72
SCH73 13.98 8.35
DETSB 17.91 7.91
exptl 0.23 8.12 -56.64

3-6-18-26 152°, 6-18-26-34 191°, 6-18-26-29 65°,
21-18-26-34 65°, 6-18-21 113°, 6-18-26 119°
ALL71 7.08 7.85

3-6-18-26 194°, 6-18-26-34 305°, 6-18-26-29 182°,
21-18-26-34 175°, 6-18-21 112°, 6-18-26 118°
WHI77 11.80 9.28

Table IV (Continued)

2,2,4,4-tetramethylpentane, C3C6(C8)(C13)C18C22(C24)(C29)C34
3-6-18-22 168°, 6-18-22-34 168°, 3-6-18 108°, 6-18-22 129°, 18-22-34 108°
DETSB 18.02 6.90
WHI77 8.13 5.23
SCH73 11.68 6.26
ALL71 4.47 6.56
exptl 0.00 8.03 -57.83

3,3,5,5-tetramethylheptane, C3C6C10(C12)(C17)C22C26(C28)(C33)C38C42
3-6-10-22 188°, 6-10-22-26 311°, 10-22-26-38 311°, 22-26-38-42 188°, 3-6-10 118°, 6-10-22 111°, 10-22-26 130°, 26-28-42 118°
DETSB 23.11 10.42
WHI77 11.68 8.56
exptl 0.39 9.64 -66.10

3-6-10-22 177°, 6-10-22-26 165°, 10-22-26-38 51°, 22-26-38-42 173°, 3-6-10 120°, 6-10-22 108°, 10-22-26 131°, 26-28-42 118°
DETSB 23.54 10.85
WHI77 12.12 9.00

3-6-10-22 177°, 6-10-22-26 167°, 10-22-26-38 170°, 22-26-38-42 293°, 3-6-10 120°, 6-10-22 107°, 10-22-26 131°, 26-28-42 119°
DETSB 23.82 11.13

3-6-10-22 178°, 6-10-22-26 167°, 10-22-26-38 165°, 22-26-38-42 59°, 3-6-10 120°, 6-10-22 108°, 10-22-26 131°, 26-28-42 118°
DETSB 23.37 10.68

3-6-10-22 178°, 6-10-22-26 167°, 10-22-26-38 167°, 22-26-38-42 177°, 3-6-10 120°, 6-10-22 108°, 10-22-26 132°, 26-28-42 120°
DETSB 23.93 11.24

3-6-10-22 186°, 6-10-22-26 286°, 10-22-26-38 167°, 22-26-38-42 177°, 3-6-10 118°, 6-10-22 111°, 10-22-26 132°, 26-28-42 120°
DETSB 23.70 11.01

3-6-10-22 177°, 6-10-22-26 165°, 10-22-26-38 289°, 22-26-38-42 304°, 3-6-10 120°, 6-10-22 107°, 10-22-26 131°, 26-28-42 119°
DETSB 23.49 10.80

2,2,4,4,5-pentamethylhexane, C3C6(C8)(C13)C18C22(C24)(C29)C34(C37)C42
3-6-18-22 169°, 6-18-22-34 167°, 18-22-34-42 58°, 6-18-22 130°
DETSB 24.77 11.30
WHI77 12.47 9.13
exptl 0.24 10.80 -67.10

3-6-18-22 164°, 6-18-22-34 54°, 18-22-34-42 189°, 6-18-22 131°
DETSB 25.01 11.54
WHI77 12.38 9.04

3-6-18-22 181°, 6-18-22-34 255°, 18-22-34-42 184°, 6-18-22 134°
DETSB 28.86 15.39

3-6-18-22 189°, 6-18-22-34 196°, 18-22-34-42 200°, 6-18-22 131°
DETSB 25.92 12.45

3-6-18-22 192°, 6-18-22-34 71°, 18-22-34-42 183° 6-18-22 130°
DETSB 25.06 11.59

3-6-18-22 169°, 6-18-22-34 163°, 18-22-34-42 185°, 6-18-22 132°
DETSB 25.26 11.79

[a] Entries are as follows: First line contains name of compound, structural description with arbitrary numbering. Next line defines torsions and angles. Subsequent lines give the force field,[1] the raw steric energy, and the formal steric enthalpy based on 0.7/1.4 entries in Table I; exptl is the experimental value of the FSE for the conformer of minimum energy; the SM correction and the enthalpy of formation at 298 K are also given.

Schleyer reports geometries derived from ALL71, SCH73, and the Boyd force fields.[3] Hagler and Lifson present recalculations based on UBCFF and VCFF. The Hagler and Lifson study focused on vibrational spectra.[24] In this study we have made calculations with WHI77 and DETSB and have compared the resulting geometries with the literature data and with data DeTar and Tenpas had obtained some years ago with ALL71, SCH73, and the Bartell force field. The several force fields give geometries that differ in detail, but no one force field is clearly superior in this respect. There are a few reports of steric energies; in addition to the Allinger values cited above Schleyer reports steric energies of 49.61 based on SCH73 and 31.28 based on ALL71. The former SE value is 1.4 kcal/mol larger than obtained by Tenpas with the same force field. Table IIA, and the discrepancy illustrates some problems with the earlier evaluations of SE's. The latter value is in reasonably close agreement with the Tenpas value.

Conformations and Formal Steric Enthalpy. "Steric strain" in acylcic alkanes arises structurally from branching, particularly multiply adjacent branching. The physical origin of strain in acyclic molecules is van der Waals repulsion between remote groups. These nonbonded repulsions are relieved in part by angle and torsional deformations and to a lesser extent by bond lengthening.

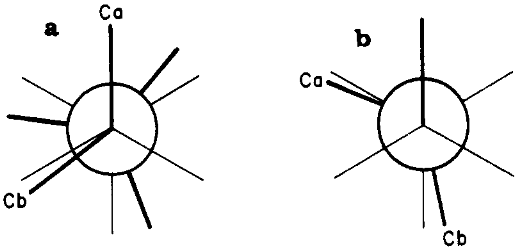

Figure 1. (a) Newman projection of one of several conformers of the pentaalkyl substructure as in 2,3,3-trimethylpentane. In all conformers the dihedral angle defined by C–C axis–C_a and C–C axis–C_b is about 130° instead of the nominal 120°. In the conformation shown the torsion indexed on the bottom alkyl group is 152° relative to C_a instead of the nominal 180°, a 28° displacement. The angles to the C atoms of the axis open to about 115° from the normal 112–113°. Other adjacent angles may be much larger. (b) Typical trialkyl substructure of isoalkanes. The dihedral angle is 123° and the torsion is 171° instead of the nominal 180° a 9° displacement.

Torsional deformations assume two forms, group rotation and "spreading" of a dihedral angle. For example, in the trialkyl substructure of Figure 1 the dihedral angle between the planes defined by C–C axis–C_a and C–C axis–C_b opens out to about 123° from the normal 120°, while in the pentaalkyl substructure it opens to about 130°. There is also usually a rotation from the staggered torsion as shown in Figure 1. The pentaalkyl substructure is common to 2,2,3-trimethylbutane, 2,2,3-trimethylpentane,

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(24) Hagler, A. T.; Stern, P. S.; Lifson, S.; Ariel, S. *J. Am. Chem. Soc.* **1979**, *101*, 813.

2,2,3,4-tetramethylpentane, and 2,2,4,4,5-pentamethylhexane. For the hexaalkyl substructure the dihedral angles tend to be nearly 120° but the torsion may deviate from the 60° staggered value. The torsions are reported in part in Table IV and in full detail in the supplementary material.[20]

Angle opening is effective in relieving unfavorable van der Waals contacts at a vertex carbon bearing one or two hydrogen atoms. It is not effective at a quaternary carbon. The force fields used in the present study all yield values of 112–113° for normal CH_2–CH_2–CH_2 angles. Substitution on the end carbon atoms causes angle opening which reaches 128–129° for di-*tert*-butylmethane. For isoalkanes the angle opens to 114–115°; for neoalkanes the angle opens to 117–118°. For most alkanes similar geometries are given by all four force fields; all angles, for example, generally agree to within 1°. Torsions show somewhat more variability, and the extent of variability depends on the rigidity of the molecule. For a crowded molecule such as 2,2,4,4-tetramethylpentane torsions predicted by the different force fields are consistent within 1°. Moreover, the difference of any pair of torsions is 120°. However, less restricted molecules may show torsional variations of up to 5° from one force field to another.

Klahn[18] has presented a useful description of relationships among angles at carbon both in terms of orbital angles and in terms of geometrical angles. A large angle reflects a pair of orbitals having large s-components. Effective symmetry at the CH carbon atom of isoalkanes (C6 in Table IV) is C_s, as is effective symmetry at the adjacent carbon (C14). Effective symmetry at the quaternary carbon atom (C6) of neoalkanes is C_{2v} and at the adjacent carbon atom (C18) it is formally C_s. However, the spread in angle values for four angles is only 1°, from 107.4° to 108.5°, at C18, and the symmetry is thus effectively C_{2v} here also.

The two ends of 2,5-dimethylhexane are independent and both have the normal geometry of an isoalkane. However, 2,4-dimethylpentane has direct interaction between the two isoalkyl groups and a central angle of 117–118°; the torsions to terminal methyls are not quite 180°. For di-*tert*-butylmethane (2,2,4,4-tetramethylpentane) the effective symmetry is C_s at the central carbon and nearly C_s at the quaternary carbons. The central angle is 128–129° and the torsions are 49°, 168°, and 286°, (dihedral angles not quite 120°), the four force fields giving concordant values within 0.5°. The related 3,3,5,5-tetramethylheptane has a similar geometry. The central angle is slightly larger, 129–130°, and the central torsions are some 10° off from the 60–180–300° minima.

Ramachandran[25,26] type diagrams have been presented in a useful recent publication[19] that summarizes steric energies of all conformers of 2,2,4,4-tetramethylpentane (di-*tert*-butylmethane). For the global minimum the reported central angle is 124.3° and the reported "ϕ" value is 46.45°. The average values given by the four force fields we have used are 128.5° and 47.6°. The authors report a steric energy of 127.702 kcal/mol, but there is no way to relate this value to results of other calculations.

Table V. Gauche Interaction Energies from Molecular Mechanics

	WHI77[a]	DETSB[b]	ALL71[c]	SCH73[c]
butane				
t	0.0	0.0	0.0	0.0
g	0.66		0.69	0.92
pentane				
t	0.0	0.0	0.0	0.0
tg	0.64	0.51	0.72	0.94
g^+g^+	1.22	0.97	1.21	1.75
g^+g^-	2.27	2.29	2.60	3.07
hexane				
ttt			0.0	0.0
ttg			0.69	0.92
tgt			0.74	0.96
g^+tg^+			1.21	1.77
g^+tg^-			1.62	1.98
tg^+tg^+			1.19	1.72
$g^+g^+g^+$			1.65	2.48
tg^+g^-			2.54	3.06
$g^+g^+g^-$			3.29	3.99
$g^+g^-g^+$			4.75	5.28
pentamethylene				
tt	0.0	0.0		
tg	0.50	0.33		
g^+g^+	1.16	0.82		
g^+g^-	1.25	1.07		

[a] Calculated in this study; ref 4. [b] Calculated in this study with new force field. [c] From ref 34.

We have not attempted to explore the complete set of local minima for the more highly substituted alkanes. For 3,5,5,5-tetramethylheptane as an example there are 25 distinct staggered conformers, not separately counting enantiomers. Many of these have multiple local minima. In Table IV we give data for five of these.

Gauche Enthalpies and Statistical Mechanical Corrections. One of the major concerns in treating steric effects theoretically is to develop simplified approaches wherever applicable. In the present study we have explored the usefulness of gauche interaction enthalpies as estimates of FSE's. Gauche enthalpies are presented in Tables IIA and IIB. Additivity is followed down through 3,3-dimethylhexane, but deviations occur for more crowded alkanes. The column labeled Δ(exptl–gauche) provides a measure of the nonadditivity, which may be called steric crowding. For the crowded compounds in Table IIA the gauche enthalpy estimate times 1.4 reproduces FSE values within 15% for most of the compounds; values for 2,2,3,3-tetramethylpentane and for 3,3,5,5-tetramethylheptane show larger discrepancies. The related problems of predicting ΔH_f data have been treated by more complicated protocols that give considerably more accurate results.[12]

Experimental values of gauche enthalpies for alkanes are rather uncertain, estimates ranging from about 0.5 kcal per mole to more than 1 kcal per mole.[9,14,28,29] The value of 0.7 which we have adopted lies within the range usually used.

In Table V we summarize the steric energies of all conformers of butane, pentane, and hexane as calculated by several force fields. Some of these data have been taken from DeTar.[6] The steric energies obtained with ALL71

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(25) Ramachandran, G. N.; Ramakrishnan, C.; Sasisekharan, V. *J. Mol. Biol.* **1963**, *7*, 95.

(26) The Ramachandran maps have been widely used. See, e.g., ref 27.

(27) Scott, R. A.; Scheraga, H. A. *J. Chem. Phys.* **1966**, *44*, 3054.

(28) Bradford, W. F.; Fitzwater, S.; Bartell, L. S. *J. Mol. Struct.* **1977**, *38*, 251.

(29) Bartell's estimate of the populations of gauche and s-trans butane gives a free energy value of 0.497 ± 0.22; Benson uses 0.80; the force fields used in the present study give values of 0.5–0.9. In another article Bartell[30] quotes and bases on analysis of gauche effects on a value of 0.966 derived by Verma et al.[31] Jorgensen computes much higher values which do not agree well with other data.[32] Benson also has discussed the assignment of gauche enthalpies.[14]

(30) Bartell, L. S. *J. Am. Chem. Soc.* **1977**, *99*, 3279.

(31) Verma, A. L.; Murphy, W. F.; Bernstein, H. J. *J. Chem. Phys.* **1974**, *60*, 1540.

(32) Jorgensen, W. L.; Irbrahim, M. *J. Am. Chem. Soc.* **1981**, *103*, 3976.

for the several conformers can be reproduced by a summation based on three assumed gauche enthalpy constants. Thus the gauche enthalpy of any conformer is given by 0.72 times the number of gauche interactions plus an additional increment of 1.25 times the number of g^+g^- or g^-g^+ sequences minus a decrement of 0.25 times the number of g^+g^+ or g^-g^- sequences. The corresponding constants for SCH73 are 0.92, 1.25, and −0.16. WHI77 and DETSB require rather smaller constants. Values of the gauche enthalpies in Table IIA are based on a simplified summation using just two constants, 0.7 for each gauche interaction plus an additional increment of 1.25 kcal/mol for each g^+g^- interaction. Gauche enthalpies in Table IIB are based on 0.3 for each gauche interaction and again a 1.25 increment for each g^+g^- interaction.

Earlier investigations of conformational populations have been given by Scheraga.[27] Flory used a simplified version of gauche enthalpies in the statistical mechanical treatment of polymers.[33] According to several force fields gauche conformers occur in pairs having torsions slightly displaced from the nominal 60° value.[27] This point is illustrated by the data in Table IV; corresponding to the reported conformer for isoalkanes with a torsion of 171° is another conformer with a torsion of 189°.

We have also used gauche enthalpies for computing the statistical mechanical correction term SM of eq 3. For most acyclic alkanes several conformations are populated at room temperature. The observed enthalpy of formation applies to the total population. In order to obtain the experimental enthalpy of formation of the single conformation of lowest energy it is necessary to estimate an appropriate SM correction. The fractional population of any conformer is proportional to its Boltzmann fraction, and the correction SM is the sum of the energies of the several conformers weighted by these fractions. In these calculations we have for practical purposes adopted the simplistic model that there is a single local energy minimum for each possible staggered conformation.

The earlier computations of DeTar[34] are not entirely error free due to an incorrect allowance for symmetry; there should be no such allowance. We have therefore recalculated all values in the present study in order to provide a consistent set. Values of SM are not very sensitive to the gauche enthalpy increments used in the additive protocol. In the SM calculations we have used 0.72 for each single gauche interaction, a 1.25 increment for each g^+g^- sequential pair, and a −0.25 increment for each g^+g^+ or for each g^-g^- sequential pair. For the nominal 0.3 set we have used 0.3, 1.25, and −0.05. Allinger has reported several SM values;[2] in general his are somewhat larger than ours.

The incremental value of SM levels off as the chain length increases. It is 0.23 for calculations based on the 0.7 gauche constants and 0.145 for the 0.3 gauche set. Based on these two different assumed gauche sets, pentane at 298 K is predicted to consist of 40% or 23% of s-trans conformer, 48% or 56% of conformers having one gauche interaction, 11% or 18% having successive g^+g^+ or g^-g^- and 1% or 2% having a g^+g^- sequence. The SM value is either 0.50 or 0.31; for octane SM is either 1.19 or 0.74.

The simplistic model errs in assuming that there is but one conformer per staggered conformation. As can be seen from examples in Table IV, for the more crowded alkanes there may be two or several local minima for a given staggered conformation. The effect of such additional minima on SM cannot be precisely predicted; to work this out in detail would require determination of the complete set of local minima, or at least those that altogether significantly affect the SM value. This number can become very large. For 3,3,5,5-tetramethylheptane, for example, there are 25 different staggered conformers and several have further local minima; some sizeable subset of these will cotribute significantly to SM. The overall correction to SM is not likely to be very large, however, due to cancellations. In a few spot calculations we found changes in SM of less than 0.1 on including representative larger sets of conformers. We conclude that uncertainties in the SM values should cause only minor uncertainties in "experimental" FSE values for the crowded alkanes.

DETSB. At the outset of the present series of studies we undertook to develop a new and possibly simplified force field designed to give good enthalpies of formation for compounds containing nitrogen and oxygen as well as carbon and hydrogen. The successes of the relatively simple Bartell force fields show that the approach should be feasible.[35,38] We prefer to base our conclusions regarding FSE values on data derived from more than one force field insofar as resources permit. DETSB was to be one of these.

The DETSB force field was to be based on three new approaches. Parameterization was to use kinetics data for esterification as well as enthalpies of formation and structural data. In view of the successes of the Lifson and the Hagler force fields with the Lennard-Jones 12-6 or 9-6 potential, we decided to adopt this nonbonded function instead of the more common exp-6 functions. We further sought to reduce the number of Lennard-Jones constants to just two by keying reference distances to an appropriate set of van der Waals radii such as the Pauling set. In practice we actually had to use four Lennard-Jones constants because of a poor original choice for the carbon radius.

For the initial stages of the parameterization we performed the least-squares adjustment only on the Lennard-Jones terms, with acyclic molecules, but using both esterification rates and enthalpies of formation data. When these first stages had been carried out, we undertook a critical examination of the characteristics of and of the performance of the resultant force field, which we now designate DETSB. This examination convineced us that the Lennard-Jones potential is a rather poor choice as a general nonbonded function since three parameters are actually needed in a nonbonded function if we are to be able to set simultaneously a repulsive energy and a gradient at some given relative nonbonded distance plus a suitable van der Waals potential well. We noted, however, that DETSB gives a considerably better account of the enthalpies of formation of acyclic molecules and of rates of esterification than do any of the other force fields with which we have worked.

Because of the deficiencies of the nonbonded functions in DETSB, we decided not to invest the further time necessary in order to develop it into a more general instrument. Since DETSB has not been calibrated with cyclic compounds, its performance with these is not very good. It was not our original intent to create a specialized acyclic force field, but in view of its very good performance with the sorts of molecules with which we are working,

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[33] Abe, A.;f Jernigan, R. L.; Flory, P. J. *J. Am. Chem. Soc.* **1966**, *88*, 631.

[34] DeTar, D. F. *Comput. lChem.* **1976**, *1*, 35.

[35] Jacob, E. J.; Thompson, H. B.; Bartell, L. S. *J. Chem. Phys.* **1967**, *47*, 3736.

[36] Bartell, L. S.; Fitzwater, S. *J. Chem. Phys.* **1977**, *67*, 4168.

[37] Gavezzotti, A.; Bartell, L. S. *J. Am. Chem. Soc.* **1979**, *101*, 5142.

[38] Bürgi, H. B. *Comput. Crystallogr., Pap. Int. Summer Sch.* **1982**, 430.

DETSB has proved to be a useful force field for our current studies.

In Table VI of the supplementary material[20] we present the details of the four force fields used in the calculations described in Tables IIA, IIB (supplementary material), and IV. All constants have been converted to the same units so that intercomparisons are possible. ALL71 uses a displaced center for computing van der Waals interactions with hydrogen atoms; this is 0.9 the distance along the C–H bond. The listing for ALL71 omits the interaction terms; these are not used in the other three force fields.

Calculations. Molecular mechanics calculations were carried out with the program MOLMEC.[39] The data in the tables in this paper were processed with data base programs on microcomputers. Copies of MOLMEC and associated programs are available on request.

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Appendix: Example Calculation of Correction Terms for FSE

To obtain the d terms for eq 6 for the DETSB force field we set up eq A1 (eq 5). We then set up the five equations

$$\text{FSE} = 0 = \text{SE} - d(\text{CH}_3)n(\text{CH}_3) - d(\text{CH}_2)n(\text{CH}_2) \qquad \text{(A1)}$$

A2. Solution gives $d(\text{CH}_3) = 0.121$ and $d(\text{CH}_2) = 0.785$.

$$\text{FSE} = 0 = 1.81 - d(\text{CH}_3) \times 2 - d(\text{CH}_2) \times 2 \qquad \text{butane}$$

$$\text{FSE} = 0 = 2.60 - d(\text{CH}_3) \times 2 - d(\text{CH}_2) \times 3 \qquad \text{pentane}$$

$$\text{FSE} = 0 = 3.38 - d(\text{CH}_3) \times 2 - d(\text{CH}_2) \times 4 \qquad \text{hexane}$$

$$\text{FSE} = 0 = 4.17 - d(\text{CH}_3) \times 2 - d(\text{CH}_2) \times 5 \qquad \text{heptane}$$

$$\text{FSE} = 0 = 4.95 - d(\text{CH}_3) \times 2 - d(\text{CH}_2) \times 6 \qquad \text{octane} \quad \text{(A2)}$$

Substituting these values into eq A3 gives d(CH) = 2.237.

$$\text{FSE} = 0.70 = 4.05 - 0.121 \times 3 - 0.785 \times 1 - d(\text{CH}) \qquad \text{2-methylbutane}$$

$$\text{FSE} = 0.70 = 4.88 - 0.121 \times 3 - 0.785 \times 2 - d(\text{CH}) \qquad \text{2-methylpentane}$$

$$\text{FSE} = 0.70 = 5.67 - 0.121 \times 3 - 0.785 \times 3 - d(\text{CH}) \qquad \text{2-methylhexane}$$

$$\text{FSE} = 0.70 = 6.45 - 0.121 \times 3 - 0.785 \times 4 - d(\text{CH}) \qquad \text{2-methylheptane} \quad \text{(A3)}$$

Substitution into A4 gives d(C) = 4.803. These are the d

$$\text{FSE} = 1.40 = 7.42 - 0.121 \times 4 - 0.785 \times 1 - d(\text{C}) \qquad \text{2,2-dimethylbutane}$$

$$\text{FSE} = 1.40 = 8.28 - 0.121 \times 4 - 0.785 \times 2 - d(\text{C}) \qquad \text{2,2-dimethylpentane}$$

$$\text{FSE} = 1.40 = 9.07 - 0.121 \times 4 - 0.785 \times 3 - d(\text{C}) \qquad \text{2,2-dimethylhexane} \quad \text{(A4)}$$

values reported in Table I. The same procedure is to be used with any other force field.

We now illustrate the calculation of the FSE value of 2,2,3,4-tetramethylpentane based on SE = 17.91, eq A5.

$$\text{FSE} = 17.91 - 0.121 \times 6 - 2.237 \times 2 - 4.803 \times 1 = 7.91 \qquad \text{(A5)}$$

These values may be compared with the entires in Table IIA.

Registry No. Ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8; pentane, 109-66-0; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; 2-methylpropane, 75-28-5; 2-methylbutane, 78-78-4; 2-methylpentane, 107-83-5; 2-methylhexane, 591-76-4; 2-methylheptane, 592-27-8; 2,4-dimethylpentane, 108-08-7; 2,5-dimethylhexane, 592-13-2; 2,2-dimethylpropane, 463-82-1; 2,2-dimethylbutane, 75-83-2; 2,2-dimethylpentane, 590-35-2; 2,2-dimethylhexane, 590-73-8; 3,3-dimethylpentane, 562-49-2; 3,3-dimethylhexane, 563-16-6; 2,2,3-trimethylbutane, 464-06-2; 2,2,3-trimethylpentane, 564-02-3; 2,2,4-trimethylpentane, 540-84-1; 2,3,3-trimethylpentane, 560-21-4; 2,2,3,3-tetramethylbutane, 594-82-1; 2,2,3,3-tetramethylpentane, 7154-79-2; 2,2,3,4-tetramethylpentane, 1186-53-4; 2,2,4,4-tetramethylpentane, 1070-87-7; 3,3,5,5-tetramethylheptane, 61868-61-9; 2,2,4,4,5-pentamethylhexane, 60302-23-0; tri-*tert*-butylmethane, 35660-96-9.

Supplementary Material Available: Formal steric enthalpies Tables IIB, IV, and VI (force fields), 2nd pictorial conformational data (33 pages). Ordering information is given on any current masthead page.

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(39) DeTar, D. F.; *Comput. Chem.* **1977**, *1*, 141.

(40) In a personal communication, Prof. C. Rüchardt reports $\Delta H = -56.4$. This corresponds to FSE = 36.89.

Substituent Effects and Isokinetic Relations in the Homolysis of Hyponitrite Esters. The Question of Free-Radical Homoconjugation

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Activation parameters for first-order homolysis of 14 *trans*-hyponitrites (alkyl, benzylic, and benzhydryl) in *tert*-butylbenzene are reported. Activation energies varied from 25–30 kcal/mol and log A/s from 13.2–15.9. These and published activation parameters on hyponitrites could be represented by isokinetic relationships, with all the compounds appearing on a single line ($r = 0.99$) in a double-log plot of calculated rate constants at 70 and 43.7 °C. The effects of α-phenyl substitution and of aromatic ring substituents on the rate constants are discussed in light of possible homoconjugation in the developing alkoxy radicals.

Substituent effects on the rates of homolytic decomposition of azo alkanes[1] and peroxides[2] have been extensively studied. The rates of homolysis of ring-substituted benzyl hyponitrites (eq 1) were measured by DeSousa, who found

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