(4.56); MS *m/e* 326 (M^+). Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 80.77; H, 9.42. Further elution yielded a semicrystalline mixture (106 mg), which was washed with MeOH to provide stilbenequinone **8** (27 mg, 1.1%) as reddish orange crystals, identical with the authentic sample (^1H NMR and TLC). Continued elution afforded a semicrystalline mixture (160 mg), which was washed with petroleum ether, yielding 2,6-di-*tert*-butyl-4-(5-methyl-2-hydroxyphenyl)-4-methylcyclohexa-2,5-dien-1-one (**23c**) (116 mg, 6.5%) as light orange crystals. Colorless crystals from acetonitrile: mp 142–145 °C; ^1H NMR δ 7.1–6.5 (m, 3 H), 6.67 (s, 2 H), 5.00 (s, 1 H, exchangeable with D_2O), 2.30 (s, 3 H), 1.60 (s, 3 H), 1.23 (s, 18 H); IR 3513, 1650, 1628 cm^{-1}; UV 280 nm (log ϵ 3.54), 239 (4.05), 222 shoulder (4.22), 203 (4.60); MS *m/e* 326 (M^+). Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C 80.69; H, 9.37. Further elution gave an oil (250 mg) which consisted of **23c** (40 mg, 2.2%) and recovered **21c**. Elution with benzene gave **21c** (1.56 g).

A similar reaction was conducted in MeOH. Dimer **3** dissolved in 100 min. The residual mixture of products was chromatographed as described above to afford **5** (1.214 g, 101%), **7** (28 mg, 1.2%), and a mixture of **9** (65 mg, 2.7%) and **24c** (15 mg, 0.8%), successively. Continued elution with petroleum ether/benzene (10:1) gave a mixture (1.25 g) consisting of **23c**, **10**, and unreacted **21c**. The mixture was chromatographed with petroleum ether on a column packed with neutral alumina (activity III, 50 g) to yield **10** (649 mg, 47%). Elution with petroleum ether/benzene (10:1) provided **23c** (308 mg, 17%). Finally, **21c** was eluted with benzene. The chromatography on SiO_2 was continued with benzene to recover **21c** (1.81 g). The reaction was also carried out in MeOH containing Et_3N (0.21 g, 2.1 mmol), and the reaction mixture was worked up similarly.

With Phenol 21d. Elution with petroleum ether afforded **5** (1.044 g, 87%) and **7** (330 mg, 14%) successively. Elution with petroleum ether/benzene (10:1) yielded 3,5-di-*tert*-butyl-4-hydroxybenzyl phenyl ether (**24d**) (416 mg, 24%) as pale yellow crystals. Colorless crystals from hexane: mp 91–92 °C; ^1H NMR δ 7.5–6.7 (m, 5 H), 7.21 (s, 2 H), 5.20 (s, 1 H), 4.89 (s, 2 H), 1.43 (s, 18 H); IR 3620 cm^{-1}; UV 277 (log ϵ 3.51), 271 (3.53), 221 (4.26), 203 (4.60); MS *m/e* 312 (M^+). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.74; H, 9.21. Further elution gave a semicrystalline mixture (460 mg) containing **24d** (330 mg, 19%) and **9** (110 mg, 4.6%). Continued elution gave a crystalline mixture (90 mg), which was washed with MeOH to provide **8** (42 mg, 1.8%). Elution with benzene afforded unreacted **21d** (1.80 g).

A similar reaction was conducted in MeOH containing Et_3N (0.21 g). Dimer **3** dissolved in 180 min. Phenol **5** (1.233 g, 102%), **24d** (355 mg, 21%), and **9** (48 mg, 2.0%) were obtained by the chromatographic procedure described above. Further elution with petroleum ether/benzene (10:1) gave **10** (732 mg, 53%). Elution with benzene gave unreacted **21d** (1.38 g).

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Estimating Entropies and Enthalpies of Fusion of Organic Compounds

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A group additivity method recently reported for estimating fusion entropies and fusion enthalpies of hydrocarbons is expanded to include both mono- and multisubstituted derivatives as well. The parameters are derived from experimental fusion enthalpies of 191 hydrocarbons and 225 monosubstituted and 233 multisubstituted hydrocarbon derivatives. Group values are provided for many structural environments. Applications of the technique are described. The average deviation between experimental and calculated fusion entropies and enthalpies obtained for monosubstituted derivatives is ±1.77 eu and ±0.49 kcal/mol, respectively. This increases to ±2.0 eu and ±0.76 kcal/mol, respectively, for multisubstituted derivatives and can be compared with values of ±1.85 eu and ±0.56 kcal/mol previously reported for hydrocarbons.

Fusion, vaporization, and sublimation enthalpies are important physical properties of the condensed phase. A variety of studies including those that reference the gas phase as a standard state require accurate values for these quantities.[1,2] Recently we described a group additivity approach to estimate fusion entropies and enthalpies of hydrocarbons.[3] In this paper, we would like to elaborate further on this method and describe how, with the introduction of some additional parameters, fusion entropies and enthalpies for a large variety of structurally diverse organic compounds can be estimated. The group additivity parameters previously generated from the experimental fusion entropies of 191 hydrocarbons are combined with additional functional group parameters generated from 225 monofunctional and 233 multifunctional hydrocarbon derivatives. Fusion enthalpy estimates are directly obtained from the fusion entropies and the experimental melting point.

As noted previously, our rationale for developing parameters for estimating fusion entropies rather than for fusion enthalpies was influenced mainly by the work of Leclercq, Jacques, and Collet[4] who investigated fusion

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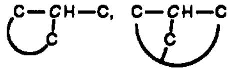
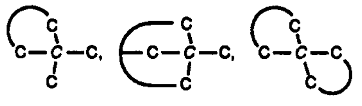
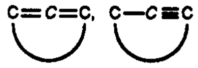
[1] See, for example: Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976.

[2] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[3] Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1990**, *55*, 3833. For a definition of terms, see also: Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1989**, *54*, 5250.

Table I. Assignment of Structural Environments

primary sp^3 carbon atom	$CH_3[C]$	*C*H_3–C
secondary sp^3 carbon atom	$CH_2[C_2]$	–*C*H_2–
tertiary sp^3 carbon atom	$CH[C_3]$	–*C*(C_3)H
quaternary sp^3 carbon atom	$C[C_4]$	*C*(C_4)
	Olefinic and Acetylenic Portions of Acyclic Hydrocarbons	
secondary sp^2 carbon	$C_uH_2[C_{sp}^{2}]$	C=*C*H_2
tertiary sp^2 carbon	$C_uH[C_{sp}^{2}C_{sp}^{3}]$	C–*C*H=C
	$C_uH[C_{sp}C_{sp}^{3}]$	C–*C*H=C=
quaternary sp^2 carbon	$C_u[C_{sp}^{2}C_2]$	C=*C*(–C)–C
tertiary sp carbon	$C_uH[C_{sp}]$	H*C*≡C
quaternary sp carbon	$C_u[C_{2sp}^{2}]$	C=*C*=C
	$C_u[C_{sp}C]$	C–*C*≡C
	Aromatic Hydrocarbons	
tertiary sp^2 carbon	$C_aH[C_{2a}]$	=C–*C*H=C
quaternary sp^2 carbon adjacent to an sp^3 carbon	$C_a[C_{2a}C_{sp}^{3}]$	=C–*C*(–CR_3)=C
peripheral quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ap}[C_{2a}C_{sp}^{2}]$[6]	
internal quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ai}[C_{3a}]$[6]	=C–*C*(–C=)=C
quaternary sp^2 carbon adjacent to sp carbon	$C_a[C_{2a}C_{sp}]$	=C–*C*(–C≡)=C
	Cyclic Hydrocarbons	
cyclic tertiary sp^3 carbon	$C_cH[C_{2c}C]$, $C_cH[C_{3c}]$	
cyclic quaternary sp^3 carbon	$C_c[C_{2c}C_2]$, $C_c[C_{3c}C]$, $C_c[C_{4c}]$	
cyclic tertiary sp^2 carbon	$C_cH[C_{2c}]$	C–*C*H=C
cyclic quaternary sp^2 carbon	$C_c[C_3]$	C–*C*(–C)=C
cyclic quaternary sp carbon	$C_c[C_{2c}]$	

enthalpies of chiral molecules and their racemic modifications. Fusion enthalpies of common organic solids average around 5–10 kcal/mol. These workers frequently found fusion enthalpies of chiral systems in which the racemic and optically active form differ by as much as 1–4 kcal/mol. Since this variation is substantial, enthalpy estimations based solely on molecular structure could expect only limited success. The development of parameters to estimate fusion enthalpies from fusion entropies, however, appeared to be more promising. Our optimism in this regard relies on the qualitative correlation observed between the magnitude of fusion enthalpies and the magnitude of the melting point of many isomeric compounds, including chiral systems.

Our parameterization of fusion entropies is based on the assumption that the contribution of a particular atom or group of atoms to the total entropy change associated in going from a rigid anisotropic solid state to the highly isotropic liquid state is fundamentally constant. Many many organic solids undergo various phase changes prior to melting. The question arises as to whether to include these transitions in the total entropy change associated with the melting process. Entropy changes associated with all these transitions have been included whenever possible in our parameterization of fusion entropies. The rationale for their inclusion is that all of these transitions are associated with an increase in randomness of the solid state and can be considered as partial transitions to the liquid state.[3,5] If this assumption is correct, it is essential to include all such transitions in estimating the total fusion entropy. *The estimation technique developed below estimates the total entropy associated with phase changes from the solid at 0 K to the liquid at the melting point.* For most compounds this is equivalent to the fusion entropy. The fusion entropy of those compounds exhibiting phase changes prior to melting will clearly be overestimated by this technique.

The general philosophical guidelines followed in developing this estimation technique was to provide the best possible correlation with the fewest number of parameters. To maintain consistency with our earlier work,[3] we have retained our previous definitions and conventions. The terms primary, secondary, tertiary, and quaternary carbon atoms, for example, are evaluated solely from the number of hydrogens attached to carbon, 3, 2, 1, 0, respectively, rather than from the number of carbon atoms as is usually the case. Values based on limited experimental data are identified by brackets and should be considered as tentative assignments.

The group additivity relationships that have previously been developed to estimate fusion enthalpies of hydrocarbons can be summarized in mathematical form by the following relationships:

acyclic and aromatic hydrocarbons

$$\Delta S_{\mathrm{fus}} = \sum_i n_i C_i G_i \tag{1}$$

cyclic hydrocarbons

$$\Delta S_{\mathrm{fus}} = [8.41 + 1.025(n - 3)] + \sum_i n_i C_i G_i \tag{2}$$

polycyclic hydrocarbons

$$\Delta S_{\mathrm{fus}} = [8.41N + 1.025(R - 3N)] + \sum_i n_i C_i G_i \tag{3}$$

Equation 1 summarizes the relationship described for estimating fusion entropies of acyclic and aromatic hydrocarbons. The n_i term refers to the number of identical groups in the molecule, and the C_i term is a coefficient that modifies each group contribution, G_i. Groups are defined structurally in Table I and assigned numerical values in

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(4) Leclercq, M.; Collet, A.; Jacques, J. *Tetrahedron* **1976**, *32*, 821; Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley and Sons: New York, 1981; Chapter 2.

(5) Ubbelohde, A. R. *Q. Rev. Chem. Soc.* **1950**, *4*, 356.

Table II. All group values are reported in entropy units, eu.[6] The subscripts c, u, and a, in Table II refer to cyclic, unsaturated, and aromatic carbon atoms, respectively. The subscripts p and i further subdivide quaternary aromatic carbon atoms into peripheral and internal aromatic carbon atoms as was previously discussed.[3,7] Subscripted carbon atoms appearing in brackets imply that the group value is dependent on the nature of adjacent carbon atoms. Values for all others groups can be used in any structural environment.

For cyclic and polycyclic molecules, eqs 2 and 3 are used. A group value for the ring atoms is calculated first from the second term in eqs 2 and 3 according to ring size n,[8] or the total number of ring atoms, R, and total number of rings, N, for polycyclic systems. Corrections for modifications from cyclic secondary sp^3 hybridized carbon are added in subsequent steps. These corrections are listed under cyclic compounds in the lower portion of Table II. Finally, the contributions of the remaining groups are added in to complete the estimation. For hydrocarbons, all the C_i terms in eqs 1, 2 and 3 equal one.

Equations 1–3 can be directly modified to include functionalized hydrocarbon derivatives using the procedure just described. The modifications result in eqs 4–7.

acyclic and aromatic molecules

$$\Delta S_{\mathrm{fus}} = \sum_{\mathrm{i}} n_{\mathrm{i}}C_{\mathrm{i}}G_{\mathrm{i}} + \sum_{\mathrm{j}} n_{\mathrm{j}}C_{\mathrm{j}}G_{\mathrm{j}} + \sum_{\mathrm{k}} n_{\mathrm{k}}C_{K}G_{\mathrm{k}} \quad (4)$$

cyclic molecules

$$\Delta S_{\mathrm{fus}} = [8.41 + 1.025(n - 3)] + \sum_{\mathrm{i}} n_{\mathrm{i}}C_{\mathrm{i}}G_{\mathrm{i}} + \sum_{\mathrm{j}} n_{\mathrm{j}}C_{\mathrm{j}}G_{\mathrm{j}} + \sum_{\mathrm{k}} n_{\mathrm{k}}C_{K}G_{\mathrm{k}} \quad (5)$$

polycyclic molecules

$$\Delta S_{\mathrm{fus}} = [8.41N + 1.025(R - 3N)] + \sum_{\mathrm{i}} n_{\mathrm{i}}C_{\mathrm{i}}G_{\mathrm{i}} + \sum_{\mathrm{j}} n_{\mathrm{j}}C_{\mathrm{j}}G_{\mathrm{j}} + \sum_{\mathrm{k}} n_{\mathrm{k}}C_{K}G_{\mathrm{k}} \quad (6)$$

$$\text{where } K = \sum_{\mathrm{k}} n_{\mathrm{k}} \quad (7)$$

The estimation of fusion entropies of substituted acyclic molecules consists in evaluating the contribution of the hydrocarbon portion of the molecule (the first term in eq 4), the contribution(s) of the carbon(s) bearing the substituent(s) (the second term), and the contribution(s) of the functional group or groups (the third term). In cyclic or polycyclic molecules, the contribution of the ring or rings is evaluated first. The quantity n in eqs 4–7 refers to the number of identical groups in the molecule and in the case of cyclic molecules, the number of atoms in the ring.[8] The hydrocarbon components are identified by the subscript i, the j subscript identifies the carbon(s) bearing the functional group(s), and the k subscript identifies the functional group(s). As noted above all C_{i} terms are numerically equal to one. Assignment of the appropriate C_{j} coefficient is determined by the structural environment of the carbon bearing the substituent as listed in the fifth column of Table II. Assignment of the appropriate C_K coefficient is determined by the nature of the functional group, k, and the total number of functional groups in the molecule according to eq 7. For monosubstituted hydrocarbon derivatives, K equals one. For compounds containing multiple substitutions, the appropriate C_K used depends on the total number of functional groups present. The only exception to this rule is for multiple fluorine substitution. Molecules containing any number of fluorine atoms are treated as having only one functional group by eq 7. Functional groups, functional group values, and functional group coefficients are reported in columns 1–6 of Table III. As in the case for C_i coefficients, many C_j and C_K values in Tables II and III also equal one. Group coefficients for some entries are not available, and those included in brackets must be considered as tentative assignments. In some instances where the appropriate coefficient is not available, it may be possible to derive some rough estimate of an appropriate group coefficient by examining the variations observed for similar functional groups if these group coefficients are available. The final column in Table III contains a summary of the number of examples used to derive each group value and group coefficient.

The group parameters for the functional groups listed in Tables II and III were obtained according to the following protocol. Data that has been critically reviewed was used in the correlations whenever possible. Most thermochemical data used was obtained from the compilation by Domalski, Evans, and Hearing.[9] Additional data was obtained directly from the literature[10] and 11 of the measurements are reported in this work. The group parameters listed in Table II were previously derived from the fusion enthalpies of hydrocarbons.[3] The experimental fusion enthalpies were grouped according to the number and kind of functional groups present. Group values for each functional group listed in Table III were evaluated by difference using the group values of hydrocarbons (Table II) to estimate the contribution of the hydrocarbon portion of the molecule to the total value. In molecules containing two or more functional groups, if the contributions of these functional groups to the total fusion entropy appeared to be simply additive, then the fusion enthalpies for these compounds were also included in the generation of the group value of the functional group and a group coefficient of one was established for the functional group. Column 7 of Table III lists the total number of entries used in the generation of each group value. In cases where the group coefficient, C_K, is 1.0, the total number of data points used to generate the functional group value can be obtained from the sum of the entries in column 7 for the particular functional group in question. Nitro groups for example, are characterized by a group coefficient of one for mono-, di-, and trisubstitution. The group value was evaluated from 4 mono-, 16 di-, and 7 trisubstituted compounds. Most but not of all of these substituents were necessarily nitro groups, although all substituents were characterized by group coefficients of one. The available data were distributed to provide statistics for as many functional groups as possible. If the contributions of a particular group appeared to be strictly additive in cases of multiple substitution, a group coefficient of one for this group was assumed in cases of multiple substitution with other substituents. For a detailed listing of this distribution, the reader is referred to the supplementary tables where all compounds used in evaluation of a group value are arranged together.

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[6] 1 eu equals 1 cal/K·mol; 4.184 J/K·mol.

[7] Examples of peripheral quaternary aromatic carbon atoms are the bridging carbons found in molecules such as naphthalene. Perylene is an example of an molecules containing both internal (2) and peripheral (6) quaternary aromatic carbon atoms.

[8] In cyclic systems, n refers to the number of equivalent methylene groups necessary to simulate the size of the ring. Corrections for other elements and substitution patterns are made at a later stage of the estimation.

[9] Domalski, E. S.; Evans, W. H.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, Suppl.1.

[10] Specific references referring to the compounds included in the correlations can be found in the supplementary tables.

Table II. Carbon Group Contributions to Fusion Entropies

acyclic hydrocarbon groups		group value G_i	group coefficients[b] C_i	group coefficients[b] C_j
primary sp^3 carbon atom	$CH_3[C]$	4.38	1.0	1.0
secondary sp^3 carbon atom	$CH_2[C_2]$	2.25	1.0	1.0
tertiary sp^3 carbon atom	$CH[C_3]$	−3.87	1.0	0.69
quaternary sp^3 carbon atom	$C[C_4]$	−9.25	1.0	0.67
	Acyclic Olefinic and Acetylenic Groups			
secondary sp^2 carbon	$C_uH_2[C_{sp}{}^2]$[a]	3.48	1.0	1.0
tertiary sp^2 carbon	$C_uH[C_{sp}{}^2C_{sp}{}^3]$, $C_uH[C_{sp}C_{sp}{}^3]$	1.16	1.0	3.23
quaternary sp^2 carbon	$C_u[C_{sp}{}^2C_2]$	−2.72	1.0	1.0
tertiary sp carbon	$C_uH[C_{sp}]$	2.6	[1.0]	[1.0]
quaternary sp carbon	$C_u[C_{2sp}{}^2]$, $C_u[C_{sp}C]$	0.52	[1.0]	[1.0]
	Aromatic Hydrocarbon Groups			
tertiary sp^2 carbon	$C_aH[C_{2a}]$	1.54	1.0	1.0
quaternary sp^2 carbon adjacent to an sp^3 carbon	$C_a[C_{2a}C_{sp}{}^3]$	−2.47	1.0	1.0
peripheral quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ap}[C_{2a}C_{sp}{}^2]$	−1.02	1.0	1.0
internal quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ai}[C_{3a}]$	0.1	[1.0]	[1.0]
quaternary sp^2 carbon adjacent to sp carbon	$C_a[C_{2a}C_{sp}]$	−0.6	[1.0]	[1.0]
	Cyclic Molecules			
contribution of the ring: $(C_cH_2)_n$	$[C_{2c}]$			
ring size: n atoms;	$\Delta S = 8.41 + 1.025[n - 3]$			
cyclic tertiary sp^3 carbon	$C_cH[C_{2c}C]$, $C_cH[C_{3c}]$	−3.82	1.0	0.76
cyclic quaternary sp^3 carbon	$Cc[C_{2c}C_2]$, $C_c[C_{3c}C]$, $C_c[C_{4c}]$	−7.88	[1.0]	1.0
cyclic tertiary sp^2 carbon	$C_cH[C_{2c}]$	−1.04	1.0	0.62
cyclic quaternary sp^2 carbon	$C_c[C_3]$	−2.8	1.0	0.86
cyclic quaternary sp carbon	$C_c[C_{2c}]$	−1.28	[1.0]	[1.0]
	Polycyclic Molecules			
total number of ring atoms: R				
number of rings: N;	$\Delta S = [8.41]N + 1.025[R - 3N]$			

[a] a, aromatic; p, peripheral; i, internal; c, cyclic; u, unsaturated. [b] Values in brackets are tentative assignments.

In all calculations, the group value was obtained by allowing its value to vary while minimizing the fractional difference between experiment and calculation by the method of least squares. In cases where multiple substitutions of the same functional group were not strictly additive (G_K unequal to one), an optimum value of G_K was obtained by a similar least-squares treatment. It was found empirically, that the best correlation of fusion entropies of compounds containing unlike functional groups is obtained when a G_K value is used based on sum of the total number of substituents rather than on the number of each individual substituent. In this sense, the effects of cumulative substitution are not strictly additive.

The group coefficients and group values were evaluated in the manner just described. It was also observed that substantial improvements in correlation could be achieved by allowing some of the C_j coefficients to vary from unity. These parameters were adjusted (by a least-squares treatment) using the entire data base, and only those coefficients were changed that substantially improved the estimations.

The application of the group values in Tables II and III to estimate fusion enthalpies according to eqs 4–7 is relatively straightforward and is similar to the procedure previously reported for hydrocarbons.[3] The functional groups in Table III are arranged according to group types. Type I functional groups are monodentate while type II are di- and tridentate functional groups. Of all these groups, cyclic type II groups are handled differently. The conventions used in these estimations and the circumstance and manner in which cyclic type II groups are used is described below and illustrated in the sample estimations of Table IV.

The first step in an estimation is to subdivide the target molecule into cyclic, aromatic, and acyclic components in order of decreasing priority. The cyclic component should be evaluated first followed by an evaluation of the remaining aromatic and/or aliphatic components. The estimation of the fusion entropy of cyclopentanethiol illustrates this general method. The contribution of the ring carbons is evaluated first. The carbon attached to sulfur in cyclopentanethiol is evaluated as a tertiary cyclic sp^3 carbon since it contains only a single hydrogen. The correction for this modification is obtained from Table II ($C_cH[C_{3c}]$), in which one carbon has been replaced by sulfur. The group coefficient for this carbon, C_j, is obtained from the last column in Table II, and the group value and group coefficient for the functional group is obtained from columns 2 and 3 of Table III.

The entropy of fusion of benzothiophene in Table IV is calculated in a similar manner. The contribution of the heterocyclic ring is estimated first. All heterocyclic pseudoaromatic rings such as found in thiophene, furan, and pyrrole are treated as cyclic alkanes. Aromatic heterocyclic molecules such as pyridine and pyrazine are evaluated as aromatic compounds as discussed below.[11] The heterocyclic ring in benzothiophene is first treated as a cyclopentane, corrected for the cyclic sulfur atom and according the priority previously stated regarding cyclic ring carbons, the two sp^2 carbons common to both the aromatic and the thiophene ring are evaluated as cyclic quaternary sp^2 hybridized carbon atoms. Although both these atoms are characterized by the same group value, their group coefficients differ as a result of the sulfur atom. The remaining two tertiary cyclic sp^2 carbon atoms in the five membered ring are characterized similarly. The

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(11) The term aromatic has been used in a general sense to include all fully conjugated planar nonbenzenoid aromatic systems such as azulene and acenaphthylene and should in principle include molecules such as the azaazulenes, etc.[3] Presently, there are no experimental data for such heterocyclic aromatic systems in our data base for comparison.

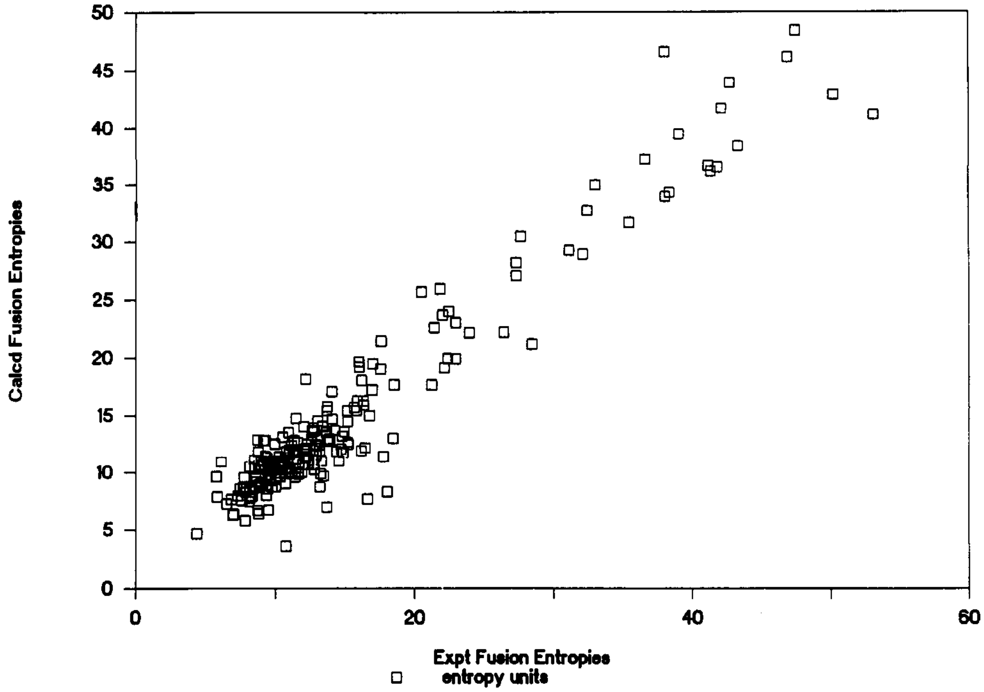

Figure 1. Calculated vs experimental fusion entropies of monofunctional hydrocarbons.

contribution of the remaining four aromatic carbons completes the estimation.

Estimation of the entropy of perfluorodecalin is similarly straightforward. Despite the fact that this molecule contains only carbon and fluorine, the molecule is treated as containing only one functional group, fluorine, attached to cyclic carbon. The contribution of the rings corrected for all the cyclic quaternary sp^3 carbon atoms completes this estimation.

The estimation of the fusion entropy of 1-naphthylamine, an aromatic amine, is calculated like the corresponding hydrocarbon. Aromatic and aliphatic compounds are evaluated from a simple additivity of each carbon in contrast to nonaromatic cyclic compounds. The only concern in this calculation is proper assignment of the aromatic carbon atom attached directly to the functional group. Whenever the functional group contains sp^2 hybridization or nonbonding electrons, we have found that the group value for a quaternary sp^2 carbon adjacent to an sp^2 carbon, $C_{ap}[C_{2a}C_{sp^2}]$, gives the best correlation.[12]

The estimation of the fusion entropy of 2-chlorobenzoic acid is an example of a molecule containing two different functional groups. The estimation follows from previous discussions. For molecules containing two functional groups, C_2 values are used for C_K in the estimation. *o*-Fluoromandelic acid is calculated similarly except here values of C_3 are used for C_K. In addition, this is a case where both the optically active (a) and racemic form (*dl*) have been measured. Although the experimental entropy values differ, this is one of many instances where the estimated fusion entropy falls in between the two experimental values. The remaining estimations in Table IV provide additional illustrations of the conventions just discussed.

The results of applying the parameters of Tables I–IV according to the procedures just described on the 444 compounds whose experimental fusion enthalpies were available to us can be seen in Figures 1 and 2. Figure 1 compares calculated and experimental fusion entropies of 226 monosubstituted hydrocarbon derivatives and a similar comparison of 218 multisubstituted compounds is shown in Figure 2. For those compounds exhibiting multiple phase changes, the comparisons in these figures are between calculated and total phase change entropies from 0 K to the melting point as noted above. The equation of the lines generated by a linear least-squares fit of the data in Figures 1 and 2 is given by eqs 8 and 10, respectively.

monofunctional compounds

$$\Delta S_{fus}(calcd) = 0.905\Delta S_{fus}(expt) + 1.07 \tag{8}$$

$$\Delta S_{fus}(calcd) = 0.958\Delta S_{fus}(expt) + 0.00 \tag{9}$$

r: 0.9597; 0.9575

standard error in ΔS_{fus}(calcd): ±2.42; ±2.48 eu

average deviation: ±1.77 eu

multifunctional compounds

$$\Delta S_{fus}(calcd) = 0.674\Delta S_{fus}(expt) + 4.5 \tag{10}$$

$$\Delta S_{fus}(calcd) = 0.952\Delta S_{fus}(expt) + 0.0 \tag{11}$$

r: 0.763; 0.691

standard error in ΔS_{fus}(calcd): ±2.24; ±2.51 eu

average deviation: ±2.03 eu

A relatively good correlation between experimental and calculated values is observed for monofunctional compounds. The correlation obtained for multisubstituted compounds (eq 10) appears poorer than for monosubstitution. However the range of experimental entropy values available (the *x* axis scale in Figure 2) is roughly half that available for the monofunctional compounds. The smaller range is probably as responsible for the poorer correlation as is the scatter of the data. The similarity in the standard errors obtained from both correlations appears consistent with this interpretation. For purposes of evaluating how much error is introduced by the assumption that the observed line passes through the origin, the lines in Figures 1 and 2 were recalculated with this additional restriction.

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[12] We would also suggest the use of the $C_{ap}[C_{2a}C_{sp^2}]$ group value in cases of adjacent sp hybridization. This suggestion however is not based on any experimental data.

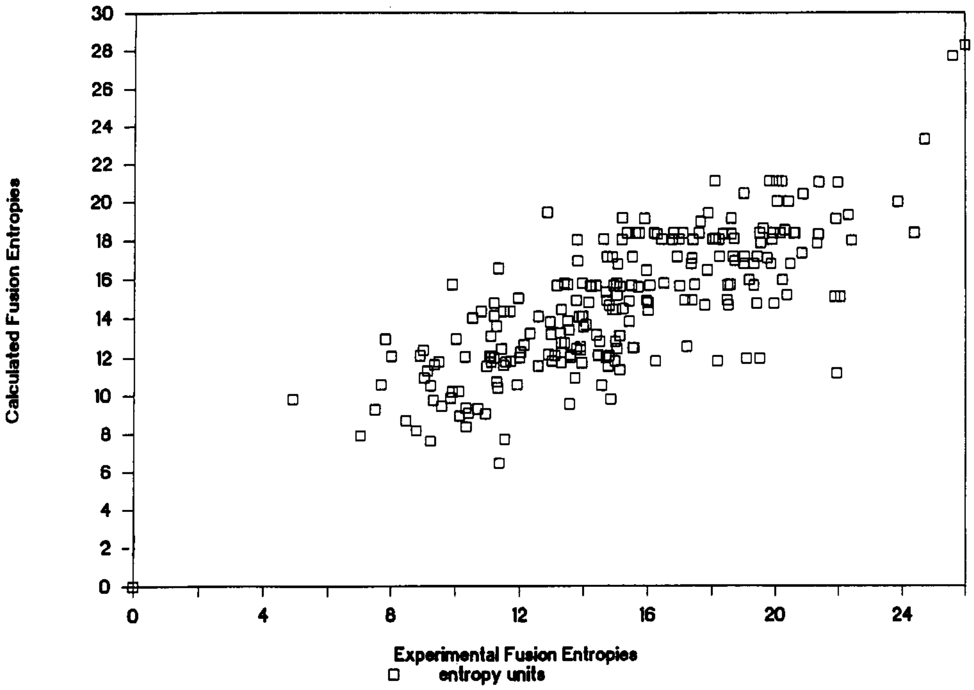

Figure 2. Calculated vs experimental fusion entropies of multifunctional hydrocarbons.

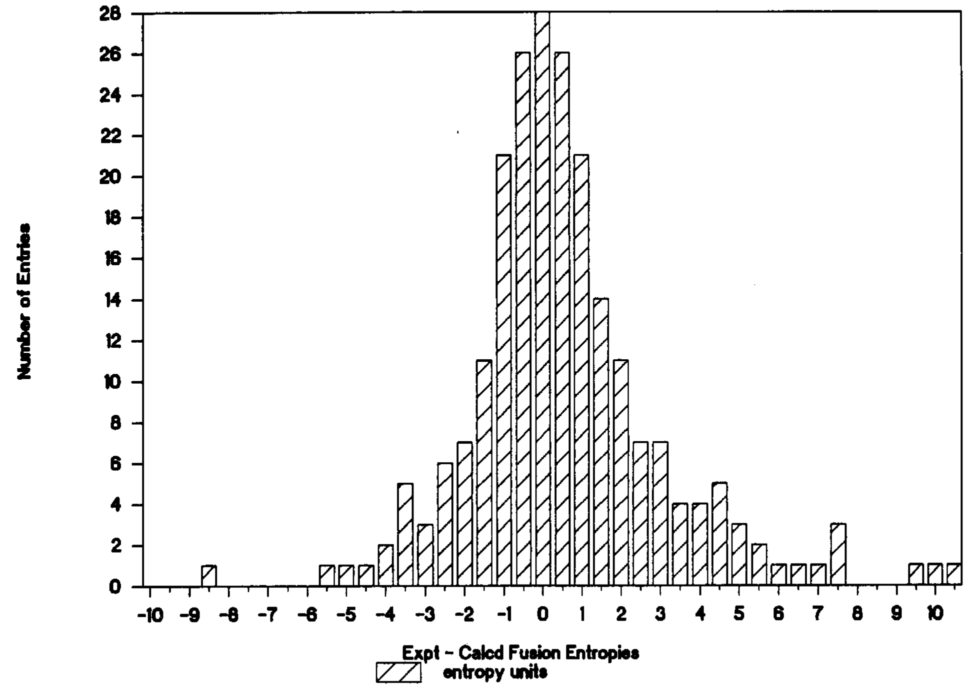

Figure 3. Distribution of errors in fusion entropy for monofunctional hydrocarbons.

Equations 9 and 11 result from least-squares treatment of the same data. The correlation coefficient and standard error obtained by this treatment are the second entry listed for each, respectively. These parameters, reported just below eqs 9 and 11, do not appear significantly affected by this assumption.

It should be noted that although the fusion entropies in Figure 1 range from about 4 to 50 eu, most values fall between 10 and 15 eu. A similar result is obtained for multisubstituted compounds although the correlation is not as good. This observation forms the basis of Walden's rule which estimates fusion entropies as approximately 13 eu.[13] As observed for hydrocarbons, Walden's rule seems to work better for highly branched and cyclic molecules but becomes a poorer approximation for linear hydrocarbons, or molecules containing long carbon chains. Functional groups on the internal portion of a carbon chain appear to have the same effect as carbon branching.

The error distribution obtained in these correlations is summarized in the histograms of Figures 3 and 4. The difference between experimental and calculated values is presented at a 0.5 eu interval. The distributions obtained for both correlations appear reasonably symmetrical.

Fusion enthalpies can now be obtained directly from the calculated entropy and the experimental melting point (K) according to eq 12. The results of comparing experimental and calculated fusion enthalpies are presented in Figures 5 and 6. In those cases where multiple phase changes are observed in the solid phase, the comparisons in the figures

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[13] Walden, P. *Z. Elektrochem.* **1908**, *14*, 713.

Table III. Functional Group Contributions to Fusion Entropies

functional group (k)	group value G_k	group coefficient (C_K)				total number of entries C_K
		C_1	C_2	C_3	C_4	
		Type I				
aldehyde	4.70	1.0				{4}
bromine	4.29	1.0	1.0	1.0	0.82	{8, 6, 8, 4}
carboxylic acid	3.56	1.0	1.83	1.88	1.72	{28, 18, 41, 2}
chlorine	2.0	1.0	2.0	2.0	1.93	{6, 23, 30, 4}
fluorine on						
sp^2 carbon	3.11	1.0	1.0	1.0	1.0	{12}
sp^3 carbon	3.52	1.0	1.0	1.0	1.0	{8}
ring carbon	3.80	1.0	1.0	1.0	1.0	{3}
hydroxyl group						
alcohol	0.27	1.0	12.6	18.9	26.4	{28, 16, 29}
phenol	3.96	1.0	1.0	[1.0]	[1.0]	{9, 12, 1}
iodine	4.05	[1.0]	[1.0]			{1, 1}
nitrile	2.30	1.0	1.4			{6, 5}
nitro group	4.15	1.0	1.0	1.0		{4, 16, 7}
primary amide	6.26	1.0	1.0			{4, 5}
primary amine						
aromatic	3.70	[1.0]	1.0			{3, 12}
aliphatic	3.88	1.0	1.82			{6}
thiols	4.30	1.0	[1.0]			{17, 1}
urea, monoalkyl	6.16	1.0				{6}
		Aromatic Type II				
aromatic heterocyclic nitrogen	1.75	1.0	[1.0]	[1.0]		{5, 2, 1}
		Acyclic Type II				
secondary amides						
amines	−0.1	1.0	1.0			{3, 3}
secondary	−0.52	[1.0]	[1.0]			{1, 1}
tertiary	−3.8	[1.0]				{2}
carbamate	−0.14	[1.0]				{3}
carbonate	−3.38	[1.0]				{2}
disulfide	1.26	[1.0]				{3}
ester	0.88	1.0	1.0	1.0	1.0	{5, 15, 14, 13}
ether	0.26	1.0	[1.0]	1.0	[1.0]	{9, 4, 10, 1}
ketone	0.75	1.0	1.0			{13, 7}
sulfide	1.72	1.0			[0.36]	{10, 0, 0, 3}
sulfone	0.78	[1.0]				{4}
		Cyclic Type II				
cyclic amine						
secondary	0.44	[1.0]				{2}
tertiary	−4.08	[1.0]	[1.0]			{1}
tertiary sp^2	0.40	[1.0]	[1.0]			{0, 2}
cyclic ether	0.32	[1.0]	[1.0]	[1.0]	[1.0]	{6, 2, 1, 1, 1}
cyclic ketone	−0.45	[1.0]	1.0			{2, 5}
cyclic sulfide	0.52	1.0	[1.0]			{10, 3}
lactone	−0.55	1.0	[1.0]			{6, 1}

are between calculated and total phase change enthalpy. The lines calculated by a least-squares fit of the calculated and experimental data is given by eqs 13–16.

$$\Delta H_{\mathrm{fus}} = T\Delta S_{\mathrm{fus}} \qquad (12)$$

monofunctional compounds

$$\Delta H_{\mathrm{fus}}(\mathrm{calcd}) = 0.941\Delta H_{\mathrm{fus}}(\mathrm{expt}) + 0.182 \qquad (13)$$

$$\Delta H_{\mathrm{fus}}(\mathrm{calcd}) = 0.940\Delta H_{\mathrm{fus}}(\mathrm{expt}) + 0.00 \qquad (14)$$

r: 0.9703; 0.9696

standard error in ΔH_{fus}(calcd): ±0.76; ±0.77 kcal/mol

average deviation: ±0.49 kcal/mol

multifunctional compounds

$$\Delta H_{\mathrm{fus}}(\mathrm{calcd}) = 0.794\Delta H_{\mathrm{fus}}(\mathrm{expt}) + 1.01 \qquad (15)$$

$$\Delta H_{\mathrm{fus}}(\mathrm{calcd}) = 0.956\Delta H_{\mathrm{fus}}(\mathrm{expt}) + 0.00 \qquad (16)$$

r: 0.8819; 0.8644

standard error in ΔH_{fus}(calcd): ±0.90; ±0.98 kcal/mol

average deviation: ±0.76 kcal/mol

As in the case with fusion entropies, the least-squares calculation were also repeated with the additional restriction that calculated line pass through the origin. Equations 14 and 15 are the result of treating the data in this manner. The correlation coefficient and standard error obtained are included as the second entry listed after these parameters. The standard error in ΔH_{fus} does not appear to be significantly affected by assuming a slope of one and an intercept of zero.

Histograms illustrating the distribution of errors in enthalpy for both mono- and multisubstituted compounds are given in Figures 7 and 8. As noted previously, experimental fusion entropies were obtained by summing all significant entropy changes occurring up to and including melting. Estimated fusion enthalpies were obtained in this work by multiplying the calculated entropy by the experimental melting point. For those substances exhibiting known solid–solid phase transitions, 86 out of the 460 compounds correlated, this manner of estimation will tend to overestimate the fusion enthalpies of these compounds. The histograms in Figures 7 and 8 should be significantly skewed if a significant error results from this convention.

Numerical values of the fusion enthalpy at temperatures other than fusion temperature are often needed in thermochemical calculations. Fusion enthalpies at 298 K differ

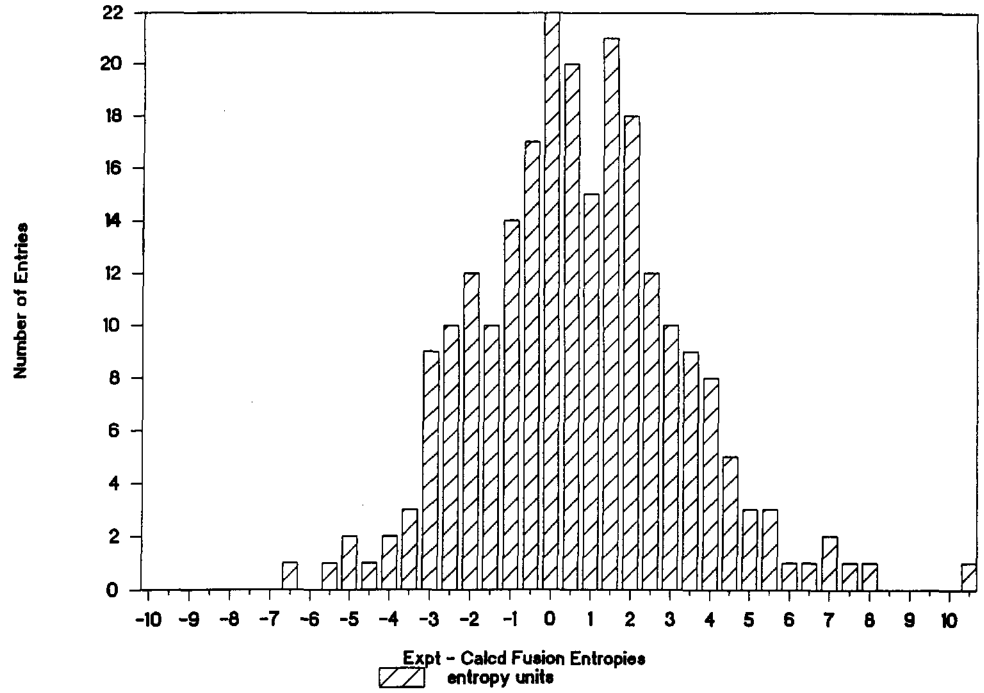


Figure 4. Distribution of errors in fusion entropy for multifunctional hydrocarbons.

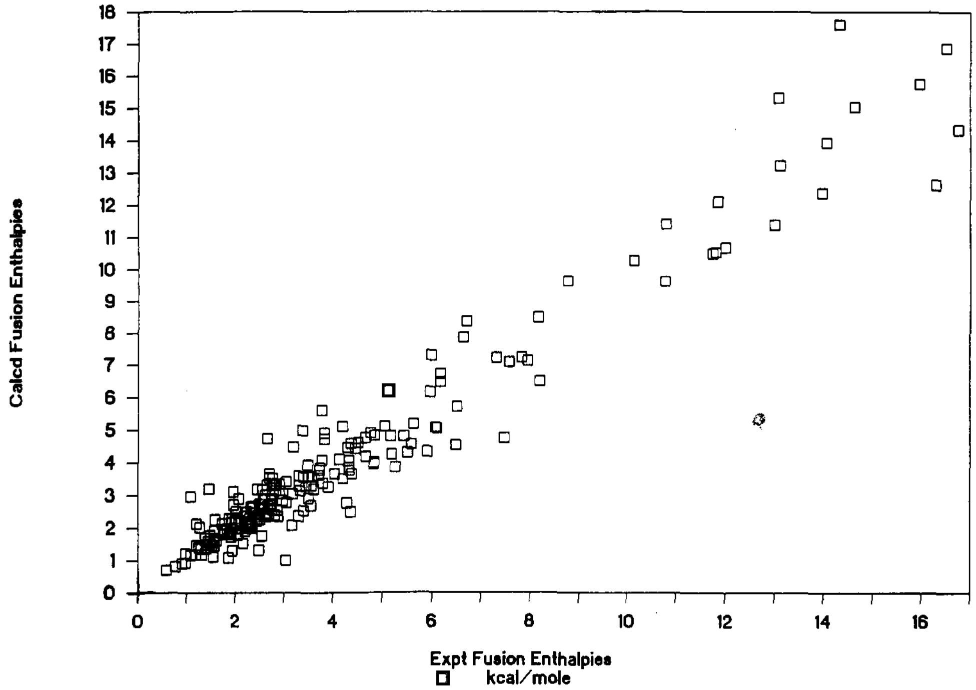
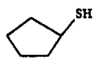
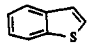
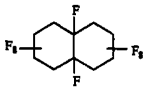
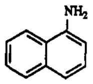
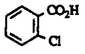
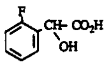
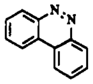
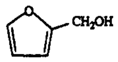
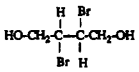


Figure 5. Calculated vs experimental fusion enthalpies of monofunctional hydrocarbons.

from those obtained at the melting point because of the differences in the heat capacities of the liquid and solid phase. Since heat capacities for both the solid and liquid phase are not presently available for most of the compounds used in this correlation, it has not been possible to correct the experimental fusion enthalpies to a standard temperature. As a consequence, the parameters in this work have been generated from experimental fusion enthalpies measured over a wide range of temperatures (the mean fusion temperature for all 651 compounds used in generating the parameters in Tables II and III (191 hydrocarbons, 225 mono- and 235 multisubstituted compounds) is 280 K). To determine how error in estimation varies as a function of fusion temperature, the difference between experimental and calculated fusion enthalpies has been plotted as a function of fusion temperature. The results are shown in Figure 9. It is evident from this graph that the scatter in the data is larger than any effect of temperature on these parameters. The divergence in the magnitude of the error as the temperature increases is mainly the consequences of how the least-square calculations were performed (vide supra).

The introduction of additional parameters would most certainly improve the correlation. In order to decrease the average error in ΔH_{fus} [between experiment and calculation] from 1.45 kcal/mol obtained from the two parameter approach of Walden to 0.63 kcal/mol [the average deviation of all 651 compounds correlated by these two methods], it has been necessary to introduce approximately 50 group parameters and to modify an additional 22 group

Table IV. Estimation of Fusion Entropies by Group Additivity

monosubstituted compounds		calculation group value (*n*) (*C*) (*G*)
	$C_5H_{10}S$ cyclopentanethiol	
	cyclopentane	[8.41] + 1.025[5 − 3]
	$C_cH[C_{3c}]$	(1) (0.76) (−3.82)
	SH	(1) (1.0) (4.3)
	ΔS_{fus}(calcd)	11.9
	ΔS_{fus}(expt)	12.0 (155.4 K)
	C_8H_6S benzothiophene	
	cyclopentane	[8.41] + 1.025[5 − 3]
	sulfide (cyclic)	(1) (1.0) (0.52)
	$C_c[C_3]$	(1) (0.86) (−2.8)
	$C_c[C_3]$	(1) (1.0) (−2.8)
	$C_cH[C_{2c}]$	(1) (1.0) (−1.04)
	$C_cH[C_{2c}]$	(1) (0.62) (−1.04)
	4 $C_aH[C_{2a}]$	(4) (1.0) (1.54)
	ΔS_{fus}(calcd)	10.2
	ΔS_{fus}(expt)	9.28 (304.5 K)
	$C_{10}F_{18}$ *cis*-perfluorodecalin	
	bicyclo[4.4.0]decane	[8.41] (2) + 1.025[10 − 6]
	10 $C_c[C_{2c}C_2]$	(10) (1.0) (−7.88)
	fluorine (ring C):	(18) (1) (3.80)
	ΔS_{fus}(calcd)	10.5
	ΔS_{fus}(expt)	9.23 (266.7 K)
	$C_{10}H_9N$ 1-naphthylamine	
	7 $C_aH[C_{2a}]$	(7) (1.0) (1.54)
	2 $C_{ap}[C_{2a}C_{sp}{}^2]$	(2) (1.0) (−1.02)
	$C_{ap}[C_{2a}C_{sp}{}^2]$	(1) (1.0) (−1.02)
	1° arom amine	(1) (1.0) (3.7)
	ΔS_{fus}(calcd)	11.8
	ΔS_{fus}(expt)	11.5 (323.2 K)
	$C_7H_5ClO_2$ 2-chlorobenzoic acid	
	4 $C_aH[C_{2a}]$	(4) (1.0) (1.54)
	2 $C_{ap}[C_{2a}C_{sp}{}^2]$	(2) (1.0) (−1.02)
	CO_2H	(1) (1.83) (3.56)
	Cl	(1) (2.0) (2.0)
	ΔS_{fus}(calcd)	14.6
	ΔS_{fus}(expt)	14.9 (413.4 K)
	$C_8H_7FO_3$ *o*-fluoromandelic acid	
	4 $C_aH[C_{2a}]$	(4) (1.0) (1.54)
	$C_{ap}[C_{2a}C_{sp}{}^2]$	(1) (1.0) (−1.02)
	$C_a[C_{2a}C_{sp}{}^3]$	(1) (1.0) (−2.47)
	$CH[C_3]$	(1) (.069) (−3.87)
	CO_2H	(1) (1.88) (3.56)
	F	(1) (1.0 (3.11)
	OH	(1) (18.9) (0.27)
	ΔS_{fus}(calcd)	14.9
	ΔS_{fus}(expt)	17.4 (*dl*, 390 K) 13.8 (a, 363 K)
	$C_{12}H_8N_2$ benzo[*c*]cinnoline	
	8 $C_aH[C_{2a}]$	(8) (1.0) (1.54)
	4 $C_{ap}[C_{2a}C_{sp}{}^2]$	(4) (1.0) (−1.02)
	2 heterocyclic N	(2) (1.0) (1.75)
	ΔS_{fus}(calcd)	14.9
	ΔS_{fus}(expt)	11.6 (432.2 K)
	$C_5H_6O_2$ furfuryl alcohol	
	cyclopentane	[8.41] + 1.025[5 − 3]
	3 $C_cH[C_{2c}]$	(3) (1.0) (−1.04)
	$C_c[C_3]$	(1) (0.86) (−2.8)
	$CH_2[C_2]$	(1) (1.0) (2.25)
	cyclic ether	(1) (1.0) (0.32)
	OH	(1) (12.6) (0.27)
	ΔS_{fus}(calcd)	14.9
	ΔS_{fus}(expt)	12.1 (258.6 K)
	$C_4H_8Br_2O_2$ 2,3-dibromo-1,4-butanediol	
 $HO\text{-}CH_2\text{-}\underset{Br}{\overset{H}{C}}\text{-}\underset{H}{\overset{Br}{C}}\text{-}CH_2\text{-}OH$	2 $CH_2[C_2]$	(2) (1.0) (2.25)
	2 $CH[C_3]$	(2) (0.69) (−3.87)
	2 OH	(2) (26.4) (0.27)
	2 Br	(2) (0.82) (4.29)
	ΔS_{fus}(calcd)	20.5
	ΔS_{fus}(expt)	19.0 (dl, 363.2 K) 20.7 (a, 338.2)

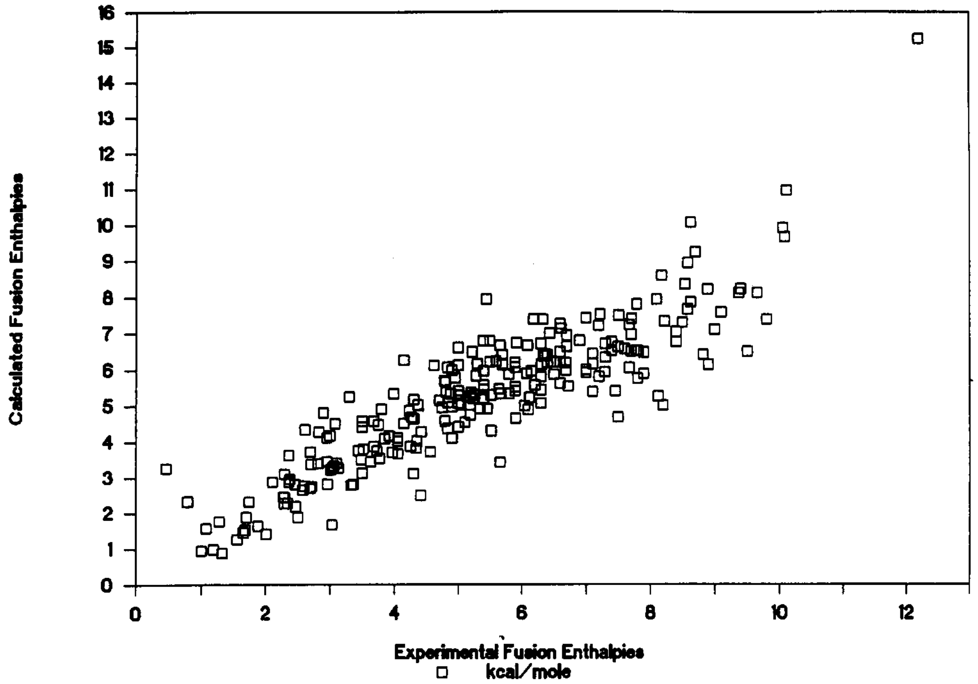


Figure 6. Calculated vs experimental fusion enthalpies of multifunctional hydrocarbons.

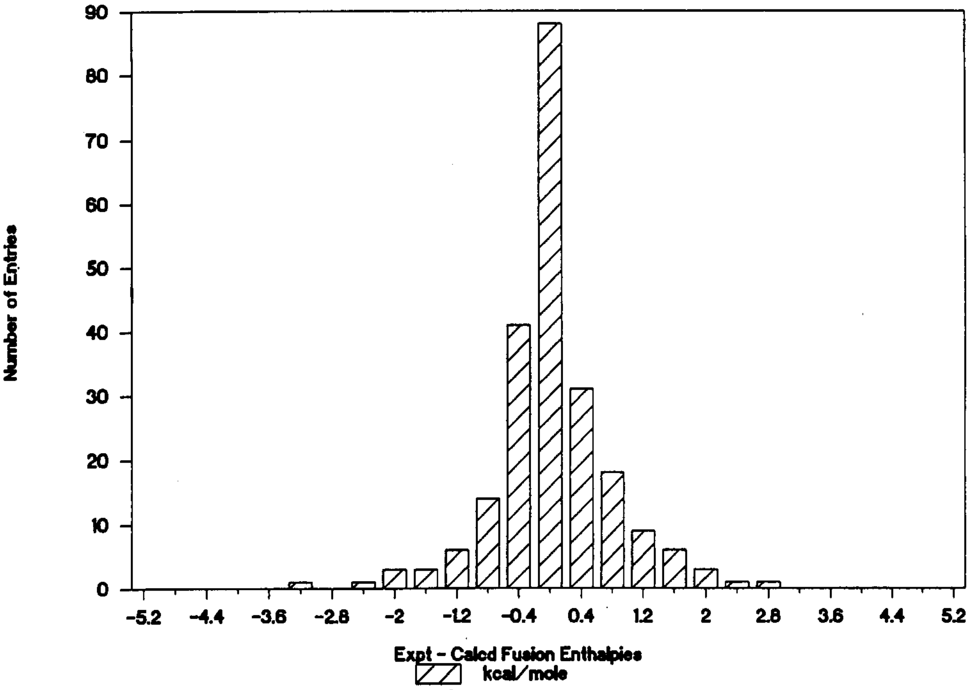


Figure 7. Distribution of errors in fusion enthalpy for monofunctional hydrocarons.

coefficients. At this rate, additional improvements in correlation to approach the uncertainty typical of most experimental fusion measurements, 0.2–0.3 kcal/mol, is likely to require the introduction of many more parameters. Such improvements should probably await a substantial increase in the available data base.

Experimental Section

Heats of Fusion. Heats of fusion were measured on a Perkin-Elmer DSC-2 Differential Scanning Calorimeter interfaced to a Compaq computer. Heats of fusion were calculated on the basis of three independent determinations on each substance. The first run was begun at room temperature or 10 K below the melting point of the sample, whichever was lower, to 10 K above the melting point at a heating rate of 10 K/min. Each sample was weighed before and after fusion to assure that sample had not been lost during heating. Samples showing a significant weight loss are so noted below and were not used in the parameterization. All samples were weighed on a Mettler H54AR scale to the nearest 0.01 mg; sample sizes of approximately 5 mg were used. Most samples were obtained from commercial sources and were characterized by NMR and melting point. Indium metal was used as the calibration standard; a heat of fusion of 6.83 cal/g was used in the calculations.[14]

In addition to the compounds measured below, naphthalene (scintillation grade, 99+%, Aldrich Chemical Company) and benzoic acid (primary standard for calorimetry, Fisher Scientific) were also measured. Five determinations of each were performed.

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[14] Groenvold, F. *J. Therm. Anal.* **1978**, *13*, 419.

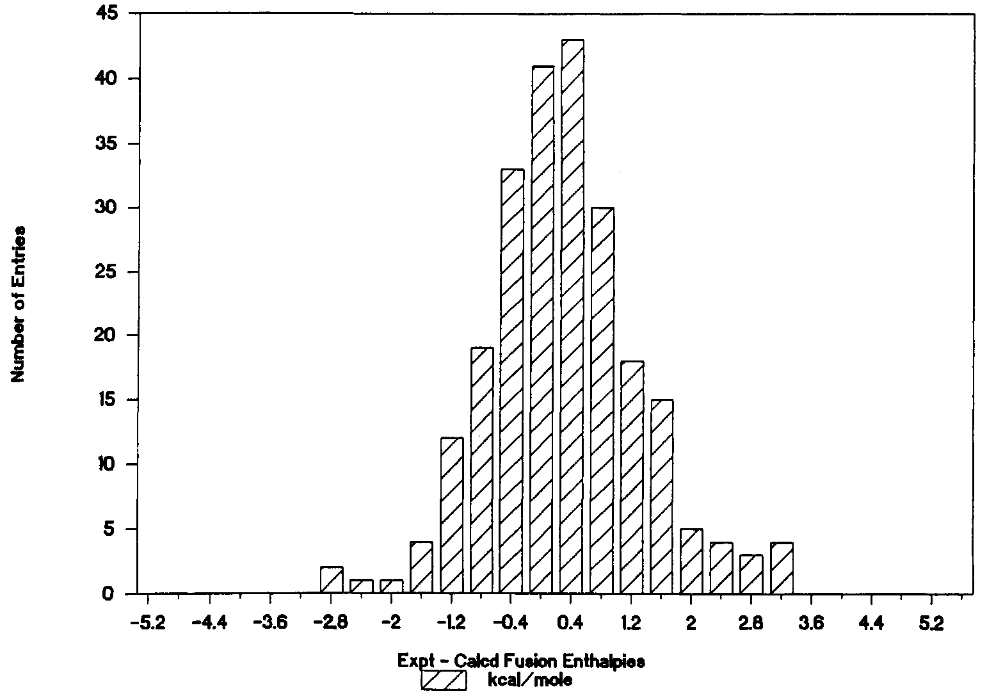

Figure 8. Distribution of errors in fusion enthalpy for multifunctional hydrocarbons.

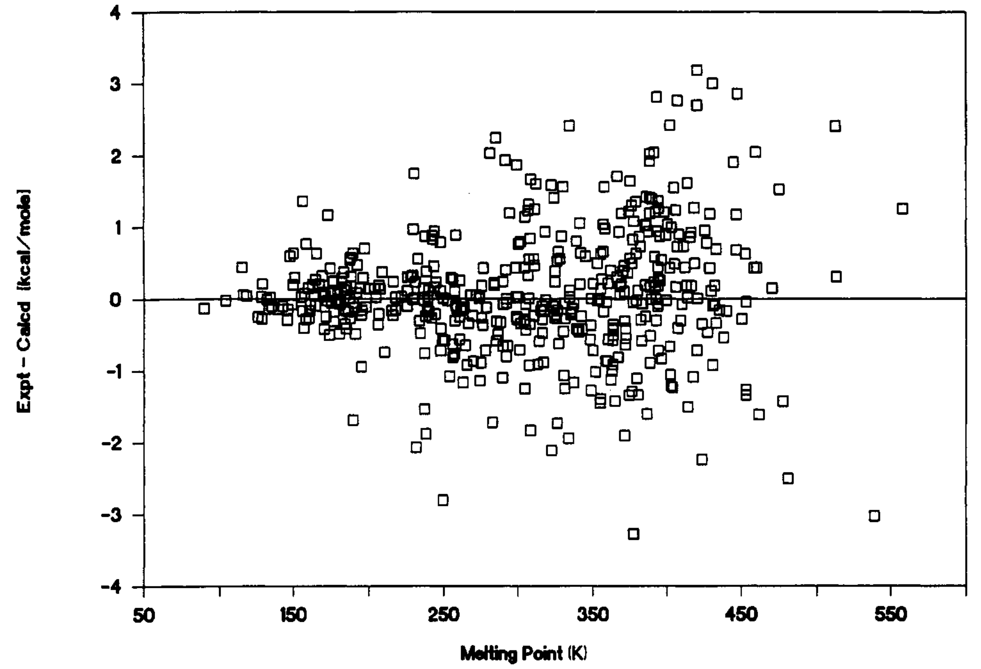

Figure 9. Observed errors in fusion enthalpy between experimental and calculated fusion enthalpies as a function of temperature.

A value of 4.8 ± 0.1 kcal/mol was measured for naphthalene (lit.[15] 4.53 kcal/mol) and 4.3 ± 0.05 kcal/mol was obtained for benzoic acid (lit.[16] 4.32 kcal/mol). On the basis of these two results we estimate our accuracy at about 6.0%.

4-*tert*-Butylbenzoic Acid. 4-*tert*-Butylbenzoic acid (99+%, Aldrich Chemical Co.) was sublimed before use: mp 163–4 °C (lit. mp 163–4 °C); ΔH_{fus} 4.28 ± 0.13 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

4-Ethylbenzoic Acid. 4-Ethylbenzoic acid (99%, Aldrich Chemical Co.) was sublimed before use: mp 111–2 °C (lit. mp 112–3 °C); ΔH_{fus} 3.36 ± 0.14 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

1-Adamantanol. 1-Adamantanol (99%, Aldrich Chemical Co.) was sublimed before use: mp 280–282 °C (sealed tube (lit. mp 280 °C)); no heat of fusion was measured (weight loss detected after fusion). A transition was detected at approximately 365 K, 3.3 ± 0.2 kcal/mol.

Methyl Palmitate. Methyl palmitate (99+%, Aldrich Chemical Co.) was used as is: mp 31–31.5 °C (lit. mp 32–34 °C); ΔH_{fus} 16.3 ± 1.2 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

2-Norbornanone. 2-Norbornanone (97%, Aldrich Chemical Co.) was sublimed before use: mp 95–6 °C (lit. mp 94–96 °C); ΔH_{fus} 0.81 ± 0.1 kcal/mol (weight loss detected after fusion); no transitions other than fusion were detected in the temperature range studied.

Octadecanamide. Octadecanamide (Technical Grade, Aldrich Chemical Co.) was purified by recrystallization (1:1 ethyl acetate–cyclohexane) and sublimed before use: mp 105.8–106 °C (lit. mp 109 °C); ΔH_{fus} 14.3 ± 0.57 kcal/mol.

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(15) Callanan, J. E.; Sullivan, S. A.; Vecchia, D. F. Feasibility Study for the Development of Standards Using Differential Scanning Calorimetry. NBS special publication 260-99, US Government Printing Office, Washington, 1985.

(16) Andon, R. J. L.; Connett, J. E. *Thermochim. Acta* **1980**, *42*, 241.

Methyl Myristate. Methyl myristate (99%, Aldrich Chemical Co.) was distilled before use: mp 19 °C (lit. mp 19 °C); ΔH_{fus} 12.0 ± 0.18; no transitions other than fusion were detected in the temperature range studied.

Dodecyl Alcohol. Dodecyl alcohol (Eastman Kodak) was recrystallized (aqueous ethanol) before use: mp 24.5–25 °C (lit. mp 22–26 °C); ΔH_{fus} 9.6 ± 0.22 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

1,3-Diphenylacetone. 1,3-Diphenylacetone (Aldrich Chemical Co.) was distilled, recrystallized (aqueous ethanol), and sublimed before use: mp 34–34.8 °C (lit. mp 35 °C); ΔH_{fus} 4.83 ± 0.2 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

Octadecyl Alcohol. Octadecyl alcohol (Eastman Kodak) was recrystallized (95% ethanol) and sublimed: mp 57–58 °C (lit. mp 59.4–59.8 °C); ΔH_{fus} 16.75 ± 0.65 kcal/mol.

2,4,6-Tri-*tert*-butylphenol. 2,4,6-Tri-*tert*-butylphenol (Aldrich Chemical Co.) was recrystallized (1:1 hexane–ethanol) before use: mp 129–130.2 °C (lit. mp 128–30 °C); ΔH_{fus} 4.65 ± 0.1 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

Cinnamyl Alcohol. Cinnamyl alcohol (Matheson Coleman And Bell) was recrystallized from hexane and sublimed before use: mp 33.9–35.9 °C (lit. mp 33 °C); ΔH_{fus} 3.76 ± 0.2; no transitions other than fusion were detected in the temperature range studied.

Thymol. Thymol (Mallinckrodt) was recrystallized before use: mp 50.5–51.5 °C (lit. mp 51.5–52 °C); ΔH_{fus} 5.3 ± 0.13 kcal/mol; no transitions other than fusion were detected in the temperature range studied.

Triphenylamine. Triphenylamine (Eastman Kodak) was recrystallized (ethyl acetate) and sublimed before use: mp 126.2–127.2 °C (lit. mp 127 °C); ΔH_{fus} 5.95 ± 0.1; no transitions other than fusion were detected in the temperature range studied.

Acknowledgment. We are grateful to the Weldon Spring Fund of the University of Missouri and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of portions of this work.

Supplementary Material Available: Tables containing the names and experimental fusion entropies and enthalpies of the 226 monosubstituted and 218 multisubstituted hydrocarbon derivatives used in this correlation as well as the values estimated by the group additivity parameters of Table II are available (44 pages). Ordering information is given on any current masthead page.

Photoreduction of π,π^* and n,π^* Triplet Carbonyls by Amines: 2-Naphthaldehyde, 2-Acetonaphthone, *p*-Aminobenzophenone, and *p*-Cyanobenzophenone. Catalysis by Aniline and Aliphatic Thiol

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Photoexcited 2-naphthaldehyde (2-NA), 2-acetonaphthone (2-AN), and *p*-aminobenzophenone (*p*-AMB), with π,π^* triplets, do not abstract H from α-C or N of a primary amine, 2-butylamine. Reductions are catalyzed by aniline plus aliphatic thiol, but not by thiol alone, to $\phi = 0.6$, 0.5, and 0.35, respectively. These triplets abstract H from N of a secondary amine, diisopropylamine, but the resulting ketyl and alkylaminyl radicals disproportionate, regenerating starting materials; these reductions are catalyzed by thiol to $\phi = 0.6$–0.5. Catalysis results from sequences of H atom transfers, from thiol to aminyl radicals, and from α-C of amines to thiyl radical, forming α-aminoalkyl radicals, which lead to final reduction products. Reduction of 2-NA by tertiary amines, triethylamine (TEA) and *N*,*N*-diethylethanolamine, is efficient in acetonitrile, $\phi = 1.5$, and less so in benzene, $\phi = 0.5$ and 0.7, respectively. Values for 2-AN are lower, 0.5–0.6 in acetonitrile, and <0.1 and 0.4, respectively, in benzene. *p*-AMB is reduced by TEA in benzene, $\phi = 0.3$. *p*-Cyanobenzophenone, with an n,π^* triplet, is reduced by these amines, in benzene, with $\phi = 0.8$ by the primary amine, $\phi = 1.4$ by TEA, and ϕ increased from 0.3 to 0.5 by thiol in reduction by the secondary amine. Relations of reactivity to carbonyl reduction potential, triplet-state energy and configuration, ionization potential of amine, and medium polarity are discussed.

Introduction

Photoreduction of aromatic carbonyl compounds by amines is affected by excited-state configuration, degree of substitution on N, and polarity of environment.[1] The reactions generally proceed via initial charge-transfer interaction, k_{ir},[2] which may be followed, to varying degree, by (i) spin inversion and return to starting materials, k_{e},[2] (ii) formation of free cation and anion radicals,[3] or (iii) hydrogen transfer from α-C, k_{h}, or from N, k'_{h} forming ketyl radical, I, and α-aminoalkyl radicals II or IV, or alkylaminyl radical, III, respectively, eq 1.[2,4] Values of k_{ir} rise with decreasing ionization potential of donors,[5–8] from primary to secondary to tertiary amines of related structure, and may also be correlated with ionization potential of donor-derived radicals.[9]

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