vacuum by heating with a heat gun, giving 20 mg (43%) **16** as an oil.

1,5-Diazatricyclo[6.2.1.0^{5,10}]undecane (19). (a) By I_2 Oxidation of 16. A solution of I_2 (41 mg, 0.16 mmol) in $CDCl_3$ (1.0 mL) was added dropwise to a solution of **16** (18 mg, 0.12 mmol) in $CDCl_3$ until an orange color persisted. Examination of the solution by ^{1}H NMR showed protonated **19** to be present. The solution was washed with aq KOH, the chloroform layer dried (K_2CO_3) and filtered, the solvent removed by rotary evaporation. Bulb-to-bulb distillation under high vacuum using a heat gun gave **19** as a clear colorless oil: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.01 [d, J = 4.2 Hz, H(10)], 3.36 [td, 13.2, 4.6, H(2/4a)], 3.22 [dd, 9.6, 5.9, H(11x)], 3.1 [m, 2H H(2/4e), H(4/2a)], 3.03 [td, 11.7, 7.4, H(6a)], 2.90 [m, H(4/2e)], 2.88 [ddd, 12.3, 7.4, 1.6, H(6e)], 2.63 [d, 9.6, H(11n)], 2.39 (br m, H(8)], 2.20 [dtt, 14.1, 12.2, 5.2, H(3a)], 1.91 [m, H(9a), H(7e)], 1.75 [m, H(7a)], 1.59 [d, 11.1, H(9b)], 0.84 [dtt, 14.2, 4.3, 2.2, H(3e)]; ^{13}C NMR ($CDCl_3$) δ 74.5 (CH[10]), 52.8 (CH_2), 51.2 (CH_2), 46.5 (CH_2), 42.6 (CH_2), 38.4 (CH_2), 32.3 (CH[8]), 31.8 (CH_2), 11.5 (CH_2[3]).

(b) By Autoxidation. O_2 was bubbled in to a solution of **16** in $CDCl_3$ (10.0 mg/0.5 mL, 0.13 M) for 1 min. **19** was detectable, although **16** was still the major product.

(c) By Quinone Oxidation. A solution of **16** (0.0073 g, 0.047 mmol) in $CDCl_3$ (0.40) was prepared and examined by ^{1}H NMR. To this solution was added a solution of benzoquinone (5.0 mg, 0.047 mmol) in $CDCl_3$ (0.1 mL). Analysis by ^{1}H NMR showed **19** to be present; no **16** remained.

Equipment. Brucker AM.500 and EM.270 NMR spectrometers, a Varian IEE-15 PE spectrometer modified as previously described,[22] and PAR electrochemical equipment were employed. Pulse radiolysis experiments were conducted using the 1.55-MeV Van de Graaf generator at the Hahn-Meitner-Institut, Berlin, using N_2-saturated water containing 0.1 M *tert*-butyl alcohol to scavenge hydroxyl radicals and 1–2 × 10^{-4} M dication.

Calculations. Calculations were carried out on a VAX 8650. MM2 calculations used a modified version of QCPE Program No. 395. It should be noted that early QCPE versions of MM2 have a mistake in the amine parameters,[12b] and give different answers as a result. Vicinal H,H couplings were calculated using a modified version of Program 3JHH, Osawa and Jaime's implementation[17b] of Haasnoot, de Leeuw, and Altona's generalized Karplus equation.[17a] The most important modification[17c] was fixing a bug in subroutine HCOREC of ref 17b in which the CH_2 symmetry correction recommended in ref 17b was improperly handled and sometimes gave wildly incorrect couplings. AM1 calculations used the AMPAC 1.00 package (*QPCE Bull.*, **1986**, *506*, 24a).

Acknowledgment. We thank the National Institutes of Health (GM-29549) and the National Science Foundation (CHE-84-15077) for partial financial support of this work. We thank Professors K.-D Asmus, M. Göbl, and J. Mönig for making the pulse radiolysis equipment at HMI-Berlin available for these experiments, and NATO for a travel grant (D.104/80) which made it possible to carry out the measurements. This work relied heavily on instruments purchased through the financial assistance of the NSF Major Instrument program. We owe special thanks to Martin Saunders for providing his stochastic search programs, which were crucial for understanding the conformations of these compounds.

Registry No. $2^{2+}[BF_4^-]_2$, 73843-85-3; **3**, 82415-33-6; **4**, 6523-29-1; $5^{2+}[BF_4^-]_2$, 82415-32-5; **6**, 82415-30-3; $7^{2+}[BF_4^-]_2$, 103094-95-7; **8**, 126579-23-5; $9^{2+}[BF_4^-]_2$, 126579-25-7; **10**, 126579-21-3; **11**, 126579-26-8; **12**, 1903-69-1; **13**, 103094-97-9; **13**-*d*, 126579-27-9; **14**, 126579-28-0; **15**, 103094-84-4; **16**, 103671-59-6; **17**, 329-94-2; **18**, 126579-29-1; **19**, 126579-22-4; $ClCH_2CH{=}CHCH_2Cl$, 764-41-0; $Br(CH_2)_3Br$, 109-64-8; 4-(*N*-methylcarbamoyl)pyridine, 6843-37-4.

Supplementary Material Available: Illustrations of the ^{1}H NMR spectra of **10**, **11**, **13**-*d*, **14**, **16**, and **19**, and ^{13}C NMR spectra of **10** and **14** (8 pages). Ordering information is given on any current masthead page.

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(22) Nelsen, S. F.; Rumack, D. T.; Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1988**, *110*, 7945.

Estimating Entropies and Enthalpies of Fusion of Hydrocarbons

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A group additivity method for estimating fusion entropies and fusion enthalpies is described. The method is based on experimental fusion enthalpies of 191 hydrocarbons. Group values are provided for most structural environments. Applications of the technique are described, and comparisons with literature values and other estimation techniques are also included. The average deviation between experimental and calculated fusion entropies and enthalpies is ±1.85 eu and ±0.56 kcal/mol, respectively.

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] The vast number of new organic compounds prepared annually far exceeds the relatively few number of thermochemical measurements reported in this same period. This divergence in numbers has directed our interest toward the development of simple empirical relationships that can be used to estimate these enthalpies.[3]

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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.; Hyman, A. S.; Ladon, L. H.; Liebman, J. F. *J. Org. Chem.* **1981**, *46*, 4295. Chickos, J. S.; Annunziata, R.; Ladon, L. H.; Hyman, A. S.; Liebman, J. F. *J. Org. Chem.* **1987**, *51*, 4311. Chickos, J. S.; Hesse, D. G.; Liebman, J. F.; Panshin, S. *J. Org. Chem.* **1988**, *53*, 3424. Chickos, J. S.; Hesse, D. G.; Liebman, J. F. *J. Org. Chem.* **1989**, *54*, 5250.

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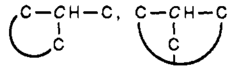
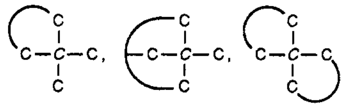
Table I. Assignment of Structural Environments

primary sp^3 carbon atom	$CH_3[C]$	$\mathit{CH}_3\mathrm{{-}C}$
secondary sp^3 carbon atom	$CH_2[C_2]$	$\mathrm{{-}}\mathit{CH}_2\mathrm{{-}}$
tertiary sp^3 carbon atom	$CH[C_3]$	$\mathit{C}\mathrm{(C_3)H}$
quaternary sp^3 carbon atom	$C[C_4]$	$\mathit{C}\mathrm{(C_4)}$
	Olefinic and Acetylenic Portions of Acyclic Hydrocarbons	
secondary sp^2 carbon	$C_uH_2[C_{sp}2]$	$\mathrm{C{=}}\mathit{CH}_2$
tertiary sp^2 carbon	$C_uH[C_{sp}2C_{sp}3]$	$\mathrm{C{-}}\mathit{CH}\mathrm{{=}C}$
	$C_uH[C_{sp}C_{sp}3]$	$\mathrm{C{-}}\mathit{CH}\mathrm{{=}C{=}}$
quaternary sp^2 carbon	$C_u[C_{sp}2C_2]$	$\mathrm{C{=}}\mathit{C}\mathrm{({-}C){-}C}$
tertiary sp carbon	$C_uH[C_{sp}]$	$\mathrm{H}\mathit{C}\mathrm{{\equiv}C}$
quaternary sp carbon	$C_u[C_{2sp}2]$	$\mathrm{C{=}}\mathit{C}\mathrm{{=}C}$
	$C_u[C_{sp}C]$	$\mathrm{C{-}}\mathit{C}\mathrm{{\equiv}C}$
	Aromatic Hydrocarbons	
teriary sp^2 carbon	$C_aH[C_{2a}]$	$\mathrm{{=}C{-}}\mathit{CH}\mathrm{{=}C}$
quaternary sp^2 carbon adjacent to an sp^3 carbon	$C_a[C_{2a}C_{sp}3]$	$\mathrm{{=}C{\cdot}}\mathit{C}\mathrm{({-}CR_3){=}C}$
peripheral quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ap}[C_{2a}C_{sp}2]$	$\mathrm{{=}C{-}}\mathit{C}\mathrm{({-}C{=}){=}C}$
internal quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ai}[C_{3a}]$	$\mathrm{{=}C{-}}\mathit{C}\mathrm{({-}C{=}){=}C}$ (see fluoranthene)
quaternary sp^2 carbon adjacent to sp carbon	$C_a[C_{2a}C_{sp}]$	$\mathrm{{=}C{-}}\mathit{C}\mathrm{({-}C{\equiv}){=}C}$
	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	$C_cH[C_{2c}]$	$\mathrm{C{-}}\mathit{C}\mathrm{H{=}C}$
cyclic quaternary sp^2 carbon	$C_c[C_3]$	$\mathrm{C{-}}\mathit{C}\mathrm{({-}C){=}C}$
cyclic quaternary sp carbon	$C_c[C_{2c}]$	

The number of reliable fusion enthalpies available has increased sufficiently to assure a statistically significant data base on which to develop molecular structure and group additivity relationships. A compilation of various critically reviewed physical properties including fusion enthalpies has recently appeared.[4] In this paper, we would like to describe a group additivity approach that has been developed to estimate the entropy associated with phase changes of hydrocarbons from 0 K to the melting point (the fusion entropy in most cases). Experimental fusion entropies of 191 organic compounds are used to evaluate group additivity parameters suitable for use in most structural environments. Combination of the experimental melting point with the estimated entropy of fusion affords an estimate of the enthalpy of fusion.

Our rationale for focusing attention on fusion entropies rather than fusion enthalpies is derived largely from the results of work reported by Leclercq, Jacques, and Collet.[5] These workers studied fusion enthalpies of chiral molecules and their racemic modifications. They frequently found fusion enthalpies of chiral systems differing from 1 to 4 kcal/mol, depending on optical purity. Since fusion enthalpies for common organic solids average typically around 5–10 kcal/mol, this variation is substantial and suggested that fusion enthalpy estimations based solely on molecular structure could expect only limited success. In order to avoid this difficulty, we focused our attention on developing an additivity method for estimating fusion entropies. Our reason for doing so is based on the differences also observed in the melting points of isomeric molecules. It is generally observed that within a set of isomeric structures, the form that exhibits the highest melting point is also characterized by the largest heat of fusion. By incorporating this empirical observation into the group additivity approach, we hoped to compensate for the differences in fusion enthalpy observed in isomeric molecules containing similar or identical molecular fragments.

An additional complication that arises in attempting to estimate either fusion entropies or enthalpies is the dilemma associated with handling the variety of solid–solid transitions that are known to occur in many molecules prior to melting. In some cases these transitions may account for a larger entropy change than occurs during melting. All of these transitions have been included in our data base whenever possible. Our rationale for including them in evaluating our group additivity parameters is as follows. All of the transitions are associated with an increase in randomness and some are the result of increases in molecular motion within the solid. They can all be considered as partial transitions to the liquid state. Since we are assuming 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, it is essential to include all such transitions in estimating the total fusion entropy.

The analysis which follows is based on the assumption that fusion entropy is a group property and can be estimated from simple additivity of the contributions of each constituent part provided that the structural environment of each group is taken into account. As in our previous work,[3] we have tried to provide the best possible correlation with a minimum number of parameters. To maintain consistency with our previous work, we have retained the previous definition of the terms primary, secondary, tertiary, and quaternary carbon atoms. Each qualifier is evaluated from the number of hydrogens attached to

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(4) Domalski, E. S.; Evans, W. H.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1984**, 13, Suppl. 1.

(5) 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.

Table II. Group Contributions to Hydrocarbon Fusion Entropies[a]

		entropy, eu[6]	number of entries
Acyclic Portions of Hydrocarbons			
primary sp^3 carbon atom	$CH_3[C]$	4.38	22
secondary sp^3 carbon atom	$CH_2[C_2]$	2.25	22
tertiary sp^3 carbon atom	$CH[C_3]$	−3.87	17
quaternary sp^3 carbon atom	$C[C_4]$	−9.25	14
Olefinic and Acetylenic Portions of Acyclic Hydrocarbons			
secondary sp^2 carbon	$C_uH_2[C_{sp}2]$	3.48	14
tertiary sp^2 carbon	$C_uH[C_{sp}2C_{sp}3]$, $C_uH[C_{sp}C_{sp}3]$	1.16	18
quaternary sp^2 carbon	$C_u[C_{sp}2C_2]$	−2.72	7
tertiary sp carbon	$C_uH[C_{sp}]$	[2.6]	1
quarternary sp carbon	$C_u[C_{2sp}2]$, $C_u[C_{sp}C]$	[0.52]	6
Aromatic Hydrocarbons			
tertiary sp^2 carbon	$C_aH[C_{2a}]$	1.54	44
quaternary sp^2 carbon adjacent to an sp^3 carbon	$C_a[C_{2a}C_{sp}3]$	−2.47	37
peripheral quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ap}[C_{2a}C_{sp}2]$	−1.02	18
internal quaternary sp^2 carbon adjacent to sp^2 carbon	$C_{ai}[C_{3a}]$	[0.1]	3
quaternary sp^2 carbon adjacent to sp carbon	$C_a[C_{2a}C_{sp}]$	[−0.6]	1
Cyclic Hydrocarbons			
contribution of the ring: $(C_cH_2)_n[C_{2c}]$			
ring size: n atoms; $\Delta S = 8.41 + 1.025[n - 3]$			7
cyclic tertiary sp^3 carbon	$C_cH[C_{2c}C]$, $C_cH[C_{3c}]$	−3.82	31
cyclic quaternary sp^3 carbon	$C_c[C_{2c}C_2]$, $C_c[C_{3c}C]$, $C_c[C_{4c}]$	[−7.88]	6
cyclic tertiary sp^2 carbon	$C_cH[C_{2c}]$	−1.04	9
cyclic quaternary sp^2 carbon	$C_c[C_3]$	−2.8	7
cyclic quaternary sp carbon	$C_c[C_{2c}]$	[−1.28]	1
Polycyclic Hydrocarbons			
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; values in brackets are tentative assignments.

carbon, 3, 2, 1, 0, respectively, rather than from the number of carbon atoms as is usually the case.

Molecular fragments for which group additivity parameters have been evaluated are listed in column 1 of Tables I and II. Column 2 identifies the atom or atoms included in each additivity term while the atom or atoms in brackets identify the number and, if necessary, the hybridization state of the atoms directly attached to each group. The subscripts c, u, and a, 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. This subdivision is discussed below and illustrated in Table IV. Subscripted carbon atoms appearing in brackets imply that the group value is dependent on the nature of adjacent carbon atoms. Values for groups containing unsubscripted carbon atoms in brackets may be used in any structural environment. The molecular fragments in this work are similar to those used by Benson in estimating gaseous heats of formation at 298 K.[1] However, sufficient differences in atom groupings do occur. In order to avoid ambiguities arising from the need to significantly modify some of the Benson grouping to suit our own needs, we have decided to devise our own system.

The structural basis of each group in this analysis is defined in Table I. The numerical contribution of each group defined in Table I to the total fusion entropy is given in column 3 of Table II; fusion entropies are reported in entropy units (eu).[6] The number of experimental data points used to generate each group value is listed in column 4. Examination of column 4 of Table II reveals that 7 of the 16 entries in this table are based on very limited amounts of data and must be considered as tentative entries. They are included in this table because most of them are unlikely to deviate significantly from this value. This permits estimation of an approximate fusion entropy. In addition, we hope that by focusing attention on these entries, this will identify the types of molecules for which sufficient data is lacking and perhaps stimulate interest in such measurements.

Most thermochemical data used in this work was obtained from the compilation by Domalski, Evans, and Hearing.[4] Some additional data on quaternary hydrocarbons was obtained directly from the literature,[7] and two of the measurements are reported in this work. Data that has been critically reviewed was used in the correlations whenever possible. The group parameters listed in Table II were evaluated by treatment of the experimental data as follows. The experimental fusion enthalpies were grouped according to structure into the general categories listed in Table III. Group values for primary and secondary sp^3 carbons were obtained by a least-squares plot of the fusion entropy of normal alkanes versus the number of methylene groups present (M). A total of 21 data entries was used. A straight line plot was obtained with the following parameters:

$$\Delta S_{fus} = [2.25\ M + 8.769]\ \text{eu};^{6}\ R = 0.9903. \qquad (1)$$

The intercept was used to evaluate the methyl group contribution (primary sp^3 carbon) while the group contribution of each methylene group (secondary sp^3 carbon) was obtained from the slope. A similar treatment of seven cycloalkane fusion entropies of ring size n versus $n - 3$ gave an equation with the following parameters:

$$\Delta S_{fus} = 1.025[n - 3] + 8.41\ \text{eu};\ R = 0.9506. \qquad (2)$$

The intercept and the size of the ring, n, was used to evaluate fusion entropies of monocyclic ring systems. This same equation can be used in polycyclic ring systems provided the atoms common to both rings are not counted twice and corrections are included for the cyclic tertiary and/or quaternary carbon atoms as described below. The correlation found in polycyclic compounds using this equation was as good as that found in monocyclic hydrocarbons.

The group values for cyclic systems and for primary and secondary sp^3 carbons were used in the determination of the remaining group parameters. Generally, the contributions of the ring and/or all primary and secondary sp^3 carbons were subtracted from the experimental fusion enthalpy. The remainder was averaged for all entries containing the structural parameter under evaluation. This value was then varied until the error was minimized by the method of least squares.[8] In some cases the ex-

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(6) 1 eu equals 1 cal/K mol; 4.184 J/K mol.

(7) Kratt, G.; Beckhaus, H.-D.; Bernlohr, W.; Ruchardt, C. *Thermochim. Acta.* **1983**, *62*, 279.

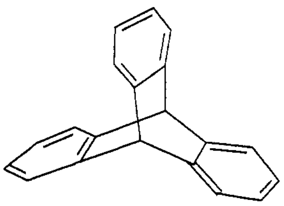
Table III. A Summary of the Origin of Parameters

parameter(s) used in the correlation	parameter(s) derived from the correlation	entries available
	Linear Acyclic Alkanes	
none	primary sp^3 carbon secondary sp^3 carbon	21
	Cycloalkanes	
none	cyclic secondary sp^3 carbon	7
	Branched Acyclic Alkanes	
primary sp^3 carbon secondary sp^3 carbon	tertiary sp^3 carbon	15
	Alkyl-Substituted Cycloalkanes	
primary sp^3 carbon secondary sp^3 carbon monocyclic ring equation polycyclic ring equation	cyclic tertiary sp^3 carbon	32
	Cyclic Quaternary Hydrocarbons	
primary sp^3 carbon secondary sp^3 carbon tertiary sp^3 carbon monocyclic ring equation polycyclic ring equation	cyclic quaternary sp^3 carbon	6
	Acyclic Olefins	
primary sp^3 carbon secondary sp^3 carbon tertiary sp^3 carbon	*secondary sp^2 carbon *tertiary sp^2 carbon	13 16
	Tri- and Tetrasubstituted Olefins	
primary sp^3 carbon secondary sp^3 carbon tertiary sp^2 carbon quaternary sp^3 carbon	quaternary sp^2 carbon	7
	Aromatic Hydrocarbons	
primary sp^3 carbon secondary sp^3 carbon tertiary sp^3 carbon tertiary sp^2 carbon tertiary sp^2 carbon secondary sp^2 carbon cyclic tertiary sp^3 carbon monocyclic ring equation	*tertiary aromatic carbon *quaternary aromatic carbon adjacent to sp^3 carbon *peripheral quaternary aromatic carbon adjacent to sp^2 carbon *cyclic quaternary sp^2 carbon	44 37 18 7
	Polycyclic Aromatic Hydrocarbons	
tertiary aromatic carbon quaternary aromatic carbon adjacent to sp^3 carbon peripheral quaternary aromatic carbon adjacent to sp^2 carbon	internal quaternary aromatic carbon	4
	Quaternary Hydrocarbons	
primary sp^3 carbon secondary sp^3 carbon secondary sp^2 carbon tertiary olefinic sp^2 carbon tertiary aromatic sp^2 carbon tertiary sp^3 carbon	quaternary sp^3 carbon	14
	Acetylenes and Allenes	
primary sp^3 carbon secondary sp^3 carbon secondary sp^2 carbon tertiary olefinic sp^2 carbon tertiary aromatic sp^2 carbon	quaternary sp carbon tertiary sp carbon quaternary aromatic carbon adjacent to sp carbon	5 1 1
	Cyclic Unsaturated Hydrocarbons	
cyclic tertiary sp^3 carbon tertiary aromatic sp^2 carbon monocyclic ring equation polycyclic ring equation	cyclic quaternary sp carbon cyclic tertiary sp^2 carbon	1 9

* Group parameters determined simultaneously.

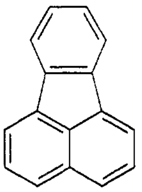
perimental data was fit to more than one parameter. These parameters are grouped together in Table III and are identified by the asterisk in column 2. In the latter case, an iteration procedure was used in the least-squares calculation. Column 1 of Table III summarizes the input parameters used in the evaluation of each group value of column 2. A detailed listing of the specific compounds used in each group evaluation is provided in the supplementary material.

The application of these group values to estimate fusion enthalpies is relatively straightforward. The examples in Table IV serve to illustrate the use of this technique. Generally the first step in the 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. 1,1-Dimethylcyclopentane serves as a useful example. The molecule contains a cyclopentane ring and two methyl groups connected by a cyclic quaternary carbon atom. The total fusion entropy is estimated by addition of the contribution of the cyclopentane ring, the two methyl groups, and the cyclic quaternary carbon, which modifies the unsubstituted five-membered ring. It is important in this estimation that the proper value for the quaternary carbon be used. Similarly, estimation of the fusion enthalpy of methylenecyclopentane, not shown in Table IV, would consist of the contributions of the five-membered ring, a cyclic quaternary sp^2 carbon, and an acyclic secondary sp^2 carbon. Estimation of the fusion enthalpy of tryptycene (1) illustrates the use of the ring equation for polycyclic molecules. The number of rings in a molecule is determined by the fewest number of carbon–carbon bonds to be broken in converting the polycyclic molecule to a completely acyclic structure. Aromatic rings are treated separately and are therefore ignored by this equation. Terms for the 6 cyclic sp^2 bridging carbons, the 12 aromatic CH groups, and the 2 tertiary sp^3-hybridized bridging carbons complete the estimation. Although the six bridging carbons are aromatic and could be classified as $C_a[C_{2a}C_{sp^3}]$, they are part of a ring and the classification of cyclic quaternary sp^2 carbons takes priority. The last example in the table demonstrates the procedure for estimating the fusion entropy of fluoranthene (2). In addition to the 10 tertiary aromatic carbons, the molecule contains 5 peripheral quaternary aromatic carbons. Examination of the parameters listed in Tables I and II under aromatic hydrocarbons identifies the entry: $C_{ap}[C_{2a}C_{sp^2}]$ as the most appropriate term for these carbons. Additionally, fluoranthene also contains one internal quaternary carbon completely encircled by other aromatic ring carbons. Since the molecule is completely conjugated, we ignore the



1

Tryptycene



2

Fluoranthene

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(8) The parameter that was minimized by the method of least squares was the fractional error in fusion enthalpy, $[\Delta H_{fus}(expt) - \Delta H_{fus}(calcd)]/\Delta H_{fus}(expt)$.

Table IV. Estimation of Fusion Entropies by Group Additivity

			experimental		
compd	group	value	transition	temp, K	ΔS, eu[6]
C_5H_8, 2,3-pentadiene					
	2 $CH_3[C]$	8.76	c/liq	145.7	10.7
	$C_u[C_{2sp}2]$	0.52			
	2 $C_u[C_{sp}C]$	2.32			
	ΔS_{fus}	11.6			10.7
C_7H_{14}, 1,1-dimethylcyclopentane					
	cyclopentane	[8.41] + 1.025 [5 - 3]			
	$C_c[C_4]$	[-7.88]	cII/cI	146.8	10.6
	2 $CH_3[C]$	8.76	cI/liq	203.6	1.3
	ΔS_{fus}	11.4			11.9
C_9H_{12}, isopropylbenzene					
	2 $CH_3[C]$	8.76			
	$CH[C_3]$	-3.87			
	5 $C_aH[C_{2a}]$	7.70			
	$C_a[C_{2a}C_{sp}3]$	-2.47	c/liq	177.1	9.9
	ΔS_{fus}	10.1			9.9
C_9H_{16}, *trans*-hexahydroindan					
	bicyclo[4.3.0]ring	[8.41]2 + 1.025[9 - 6]			
	2 $C_cH[C_{3c}]$	-7.64	c/liq	213.9	12.2
	ΔS_{fus}	12.3			12.2
$C_{10}H_8$, azulene					
	8 $C_aH[C_{2a}]$	12.32	c/liq	373.5	11.5
	2 $C_{ap}[C_{2a}C_{sp}2]$	-2.04			
	ΔS_{fus}	10.3			11.5
$C_{11}H_{24}$, 2-methyldecane					
	3 $CH_3[C]$	13.14	c/liq	224.3	26.7
	$CH[C_3]$	-3.87			
	7 $CH_2[C_2]$	15.75			
	ΔS_{fus}	25.0			26.7
$C_{20}H_{14}$, tryptycene					
	bicyclo[2.2.2]ring	[8.41]2 + 1.025[8 - 6]			
	2 $C_cH[C_{3c}]$	-7.64			
	6 $C_c[C_3]$	-16.8			
	12 $C_aH[C_{2a}]$	18.48	c/liq	527.2	13.7
	ΔS_{fus}	12.9			13.7
$C_{16}H_{10}$, fluoranthene					
	10 $C_aH[C_{2a}]$	15.4			
	5 $C_{ap}[C_{2a}C_{sp}2]$	-5.10			
	$C_{ai}[C_{3a}]$	[0.1]	c/liq	383.4	11.7
	ΔS_{fus}	10.4			11.7

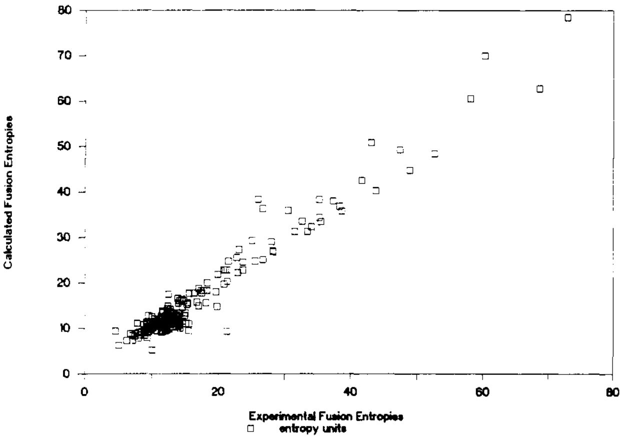

Figure 1. Calculated vs experimental fusion entropies.

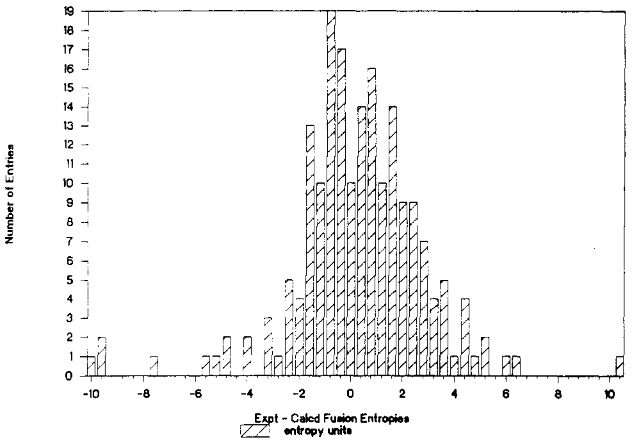

Figure 2. The distribution of errors in fusion entropies.

five-membered ring in the estimation and treat the molecule as a totally aromatic molecule.[9]

In this manner, it has been possible to estimate the fusion entropies of 192 hydrocarbons using molecular structure and the 20 parameters listed in Table I. An idea of the type of correlation achieved by this approach is obtained by comparing experimental and calculated entropies. This is shown in Figure 1. The equation of the line by a least-squares fit of the experimental data is given by eq 3.

$$\Delta S_{fus}(\text{calcd}) = 1.02\Delta S_{fus}(\text{expt}) - 0.405 \qquad (3)$$

$$r = 0.9741$$

$$\text{standard error in } \Delta S_{fus}(\text{calcd}) = 2.66 \text{ eu}$$

$$\text{average deviation} = 1.85 \text{ eu}$$

$$\text{average relative error} = 12.1\%$$

The error distribution obtained in this correlation is summarized in the histogram of Figure 2. The difference

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[9] The term aromatic is used in a general sense to include all fully conjugated planar nonbenzenoid aromatic systems as well. This includes molecules such as azulene and acenapthylene.

Table V. A Comparison of Experimental and Calculated Fusion Enthalpies

compd	transition	T_{fus}, K	exptl ΔH_{fus}, kcal/mol	group additivity: this work	group additivity: Domalski and Hearing[7]	group additivity: est by Walden's Rule
C_5H_{10}, *cis*-2-pentene	c/liq	121.8	1.70	1.62	1.81	1.58
C_5H_{12}, pentane	c/liq	143.5	2.01	2.23	2.22	1.87
C_6H_{12}, 3,3-dimethyl-1-butene	cII/cI	124.9	1.04			
	cI/liq	158.4	0.26			
	total:		1.30	1.35	2.50	2.06
C_6H_{14}, 2-methylpentane	c/liq	119.5	1.50	1.65	1.50	1.55
C_8H_8, styrene	c/liq	242.2	2.62	2.74	2.62	3.15
C_8H_{18}, octane	c/liq	216.3	4.96	4.82	4.86	2.81
$C_{11}H_{24}$, undecane	cII/cI	236.6	1.64			
	cI/liq	247.6	5.30			
	total		6.94	7.19	7.50	3.22
$C_{12}H_{10}$, biphenyl	c/liq	341.5	4.46	4.56	3.98	4.44
$C_{16}H_{34}$, hexadecane	c/liq	291.3	12.8	11.7	11.9	3.79
$C_{18}H_{12}$, triphenylene	c/liq	471.0	5.90	5.82	5.02	6.12

between experimental and calculated values is presented at each 0.4 eu interval.

A relatively good correlation between experimental and calculated values is observed. It should be noted that although the fusion entropies in Figure 1 range from about 4 to 80 eu, most values fall between 10 and 15 eu. This observation forms the basis of Walden's Rule, which estimates fusion entropies at approximately 13 eu.[10] As shown in Table V, this rule seems to work moderately well for highly branched and cyclic molecules but becomes a poorer approximation for linear hydrocarbons, or molecules containing long carbon chains.

Fusion enthalpies can now be obtained directly from the corresponding entropy and the experimental melting point (K). The results of experimental and calculated fusion enthalpies are correlated in Figure 3. The line calculated by a least-squares fit of the calculated and experimental data is given by eq 4.

$$\Delta H_{fus}(\text{calcd}) = 0.9944\Delta H_{fus}(\text{expt}) + 0.063 \quad (4)$$

$$r = 0.9733$$

$$\text{standard error in } \Delta H_{fus}(\text{calcd}) = 0.92 \text{ kcal/mol}$$

$$\text{absolute average deviation} = 0.56 \text{ kcal/mol}$$

$$\text{average relative error} = 15.4\%$$

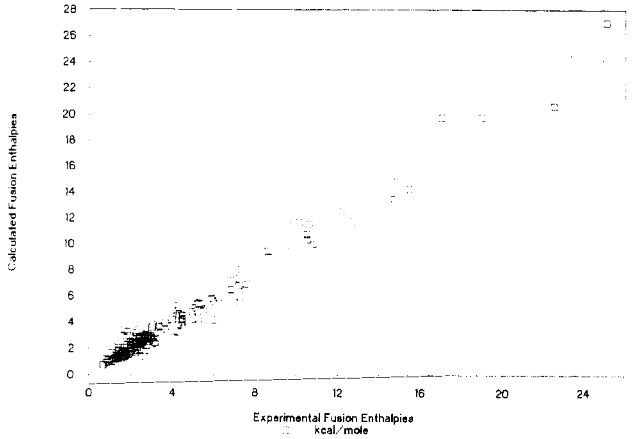

Figure 3. Calculated vs experimental fusion enthalpies.

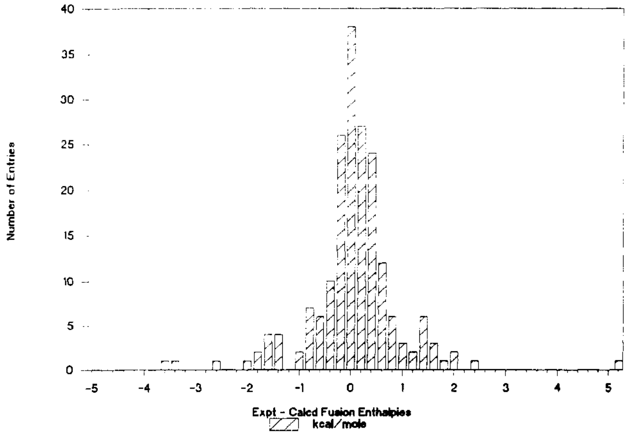

Figure 4. The distribution of errors in fusion enthalpies.

The histogram illustrating the distribution of errors in enthalpy at a 0.2 kcal/mol interval is given in Figure 4. It is significant to point out that the distribution of errors appears to be very symmetrically distributed. As noted above, experimental fusion entropies were obtained by summing all entropy changes occurring over a broad spectrum of temperatures. Fusion enthalpies are calculated in this work by multiplying the total fusion entropy by the experimental melting point. For those substances exhibiting solid–solid phase transitions, the comparisons in Figure 2 are for the total enthalpy change observed. The group values in Table I were generated to calculate the total entropy change. Since some of the entropy changes occur at temperatures below the melting point, this manner of calculating enthalpy changes should overestimate fusion enthalpies for some hydrocarbons. The error distribution should be skewed toward negative values if this factor is significant in this correlation. Examination of Figure 4

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(10) Walden, P. *Z. Elektrochem.* **1908**, *14*, 713.

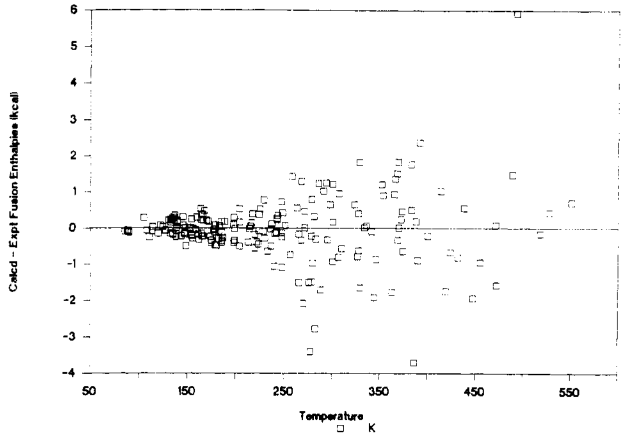

Figure 5. Errors in fusion entropies vs temperature.

shows this not to be the case despite the fact that solid-solid transitions are known for 44 of the 191 compounds used in the correlation.

Fusion enthalpies are known to be temperature dependent. Fusion enthalpies at 298 K differ from those obtained at the melting point generally because of the differences in the heat capacities of the liquid and solid phase. Since our parameters were generated from fusion entropies measured over a wide range of temperature (from 89 to 551 K with an average temperature of 224 K), we were concerned whether our error distribution showed any correlation with the fusion temperature. Figure 5 shows the difference between experimental and calculated fusion enthalpies as a function of the melting point of each individual substance used in the correlation. It is evident from the figure that the scatter in the data is larger than the effect of temperature variations on these parameters.

Relatively few other methods of predicting fusion enthalpies have been reported. Walden's Rule has been mentioned previously. Very recently, Domalski and Hearing[11] reported a group additivity approach for calculating heats of formation of hydrocarbons (ΔH_f) in the gas, liquid, and solid phases. Fusion enthalpies can in principle be extracted from the estimated differences in ΔH_f. A comparison of both of these more recent additivity approaches to those obtained by using Walden's Rule seems appropriate. The estimations of all three methods are included in Table V for some representative compounds. In general, good agreement is found between the two group additivity methods. The results obtained from Walden's Rule are clearly more qualitative. An examination of the compounds used in both the Domalski study and in our own analysis identified 93 compounds common to both studies. An average deviation of 0.52 and 0.32 kcal/mol was found between experimental and calculated values for these compounds using the Domalski–Hearing parameters and our own, respectively. The slightly larger error in the Domalski–Hearing method probably reflects the fact that fusion enthalpies in this case are calculated by taking the difference between two estimates, heats of formation in the solid and liquid phases, respectively, both large numbers. At present, the major limitation to the Domalski–Hearing method is the limited number of group parameters that are available for calculating heats of formation in both the solid and liquid phases.

As a means of evaluating the reliability of these estimation techniques, some measure of the general accuracy of experimental fusion enthalpies reported in the literature would be useful. We have calculated the average deviation observed for all multiple measurements reported on the same substance appearing in the Domalski, Evans, and Hearing compendium.[4] An average deviation of 0.2 kcal/mol was observed for 216 compounds for which multiple measurements could be found. This compares to an average deviation of 0.56 kcal/mol observed for the 191 compounds in this study. A linear regression analysis of the multiple measurements cited above versus their mean resulted in a standard error of 0.66 kcal/mol. This value can be compared to a standard error of 0.92 kcal/mol which we obtained when comparing calculated and experimental fusion enthalpies (see eq 4). We conclude that the typical uncertainty associated with this group additivity approach to estimating fusion enthalpies is roughly twice the uncertainty associated with the experimental measurements.

Our present difficulty in handling compounds exhibiting transitions in the solid phase is one possible factor responsible for the magnitude of the uncertainty of our calculated results. It is encouraging to note in this respect that the average deviation of the 44 compounds in our data base known to exhibit solid–solid phase transitions is only 0.60 kcal/mol (compared to an overall average of 0.56 kcal/mol). This suggests that other factors are also responsible for the magnitude of the error observed. As the size of data base increases, it is quite likely that improvements in correlation will be possible with the introduction of additional parameters. The applicability of this group additivity approach of estimating fusion enthalpies combined with the equations previously reported for estimating vaporization enthalpies to estimate sublimation enthalpies will be the subject of a future report.

Experimental Section

Heats of Fusion. Cyclotetradecane was purchased from Wiley Organics, and cyclotetradecadiyne was purchased from K and K Laboratories. Both were recrystallized from acetone. Their identity was confirmed by melting point and ^{1}H and ^{13}C NMR spectroscopy. Analysis by gas chromatography indicated purities of 98.9 (cyclotetradecane mp 54.8–55.4 °C (lit.[12] mp 54–55.5 °C)) and 99.9% (cyclotetradecadiyne mp 96.7–97.3 °C (lit.[12] mp 97–98 °C)). 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. Indium metal was used as the calibration standard; a heat of fusion of 6.83 cal/g was used in the calculations.[13] The DSC trace for cyclotetradecane exhibited a peak at 48 °C and melting at 55 °C. The relative areas of the two peaks were comparable but varied depending on sample history. The total area remained constant and was reproducible upon remelting and from sample to sample. A total value of 6.86 ± 0.08 kcal/mol (average deviation) was calculated from the combined areas of these two peaks.

No transitions other than melting were observed for cyclotetradecadiyne from room temperature to 97 °C. A heat of fusion of 5.40 ± 0.26 kcal/mol was calculated for cyclotetradecadiyne.

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.

Registry No. 2,3-Pentadiene, 591-96-8; 1,1-dimethylcyclopentane, 1638-26-2; isopropylbenzene, 98-82-8; *trans*-hexahydroindan, 3296-50-2; azulene, 275-51-4; 2-methyldecane,

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(11) Domalski, E. S.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, 1637.

(12) Dale, J.; Hubert, A. J.; King, G. S. D. *J. Chem. Soc.* **1963**, 73.

(13) Groenvold, F. *J. Therm. Anal.* **1978**, *13*, 419.

6975-98-0; tryptycene, 477-75-8; fluoranthene, 206-44-0; *cis*-2-pentene, 627-20-3; pentane, 109-66-0; 3,3-dimethyl-1-butene, 558-37-2; 2-methylpentane, 107-83-5; styrene, 100-42-5; octane, 111-65-9; biphenyl, 92-52-4; hexadecane, 544-76-3; triphenylene, 217-59-4; undecane, 1120-21-4.

Supplementary Material Available: Tables containing the names and experimental fusion entropies and enthalpies of the 191 hydrocarbons used in this correlation as well as the values estimated by the group additivity parameters of Table I (21 pages). Ordering information is given on any current masthead page.

Experimental Evidence for the Lack of Stereoselectivity in the Electrophilic Quench of α-Sulfonyl Carbanions

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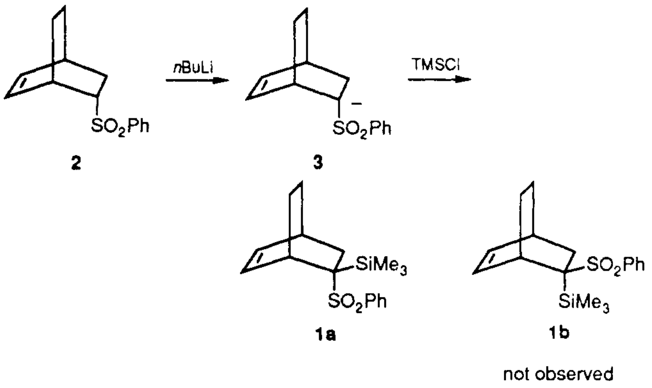
A series of α-sulfonyl carbanions was generated from the corresponding bridged bicyclic sulfones. These anions were quenched with a variety of electrophiles, and the stereoselectivities of these reactions were examined. Stereochemical assignments were based on X-ray and NMR data. It was found that factors other than the initial stereochemistry of the sulfonyl group dominated any observed stereoselectivity. Deuterium-labeling studies revealed essentially no stereoselectivity in the electrophilic quenches of the symmetrical bicyclo[2.2.2]octane system.

In connection with our interest in developing new synthetic methods utilizing novel aspects of organosilicon and organosulfur chemistry,[1] we prepared the epimeric silylsulfones **1a** and **1b**. The simplest approach appeared to be from the known[2] 5-*endo*-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (**2**) by generation of the α-sulfonyl anion **3** and subsequent quenching with chlorotrimethylsilane ((TMS)Cl).



2 **3** **1a** **1b**

Indeed Paquette[2] had demonstrated that the anion generated from the epimeric mixture of 1-methoxy-6-*endo*/*exo*-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene could be readily quenched with simple electrophiles. The endo:exo ratio of this epimeric starting material is not specifically reported, although from the preparation it is isolated as a 4.56:1 mixture of endo and exo (sulfonyl group) epimers. The products from these quenching reactions ranged between 2 and 3.7:1 mixtures of endo to exo (sulfonyl group) isomers.[2] In our system, quenching of the carbanion **3** (derived from the single epimer **2**) with (TMS)Cl gave only one product (GC analysis), **1a** or **1b** in 93% isolated yield. Recent calculations at the ab initio level by Wolfe suggest that stereoselectivity should be observed in the quenching of α-lithiosulfones,[3] and he comments that "the very limited experimental data are consistent with this conclusion". It is not feasible to carry out such calculations on systems as large as **3**. However, it is reasonable to anticipate that if the dominant influence controlling the stereochemistry of electrophilic quenching of these carbanions is the sulfonyl group itself, then Wolfe's predictions should apply in the current study. There has been much debate as to the nature of α-sulfonyl anions,[4] especially as to whether the geometry at the α-carbon is planar or pyramidal.[5] The results from most studies on the quenching of α-sulfonyl anions can be explained in terms of either an asymmetrically solvated planar carbanion or a pyramidal carbanion. There are many studies supporting either a planar[6] or pyramidal[10] geometry for the anionic site. However, the

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