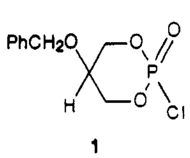
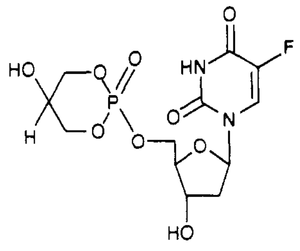
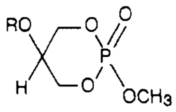


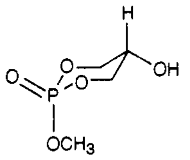
1



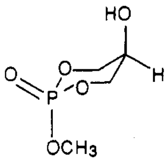
2



3, R = H
4, R = CH_2Ph



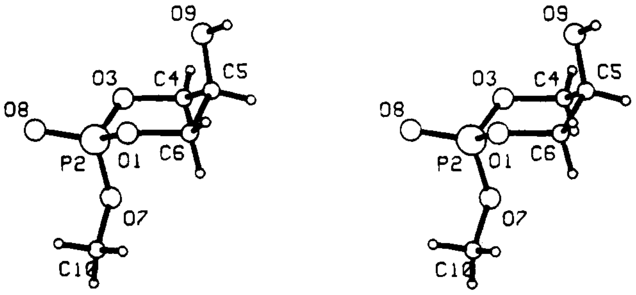
3A



3B

hospha and oxazaphospha heterocycles,[1,4] which under physiological conditions would yield the nucleoside monophosphate once the cyclic phosphotriester had penetrated the cell wall. This approach has also recently been reported by others.[5] Our derivative **2** was far too stable, and it occurred to us that if the compound reported by Denney and Varga had indeed the stereochemistry they suspected and if the corresponding nucleoside derivative were synthesized and it proved to be different from that previously reported by us,[1] it might be more labile because of the possibility of neighboring group participation by the axial hydroxyl group of the 1,3,2-dioxaphosphacyclohexane ring.

We thus prepared compound **3** first by a modification of the method previously described by us[1] from 2-*O*-benzylglycerol to give **3A** and second by the method described by Denney and Varga[2] to give **3B**. The proton NMR spectra of **3A** and **3B** were recorded at 270 MHz and ^{31}P spectra at 162 MHz with proton decoupling. The spectra from preparation **3B** clearly show that the hydroxyl group is in the axial position and the H-5 in the equatorial position is found upfield as would be expected. The axial H-4 and H-6 protons are also clearly seen downfield from the equatorial H-4 and H-6 protons. The identity of this isomer (**3B**) was confirmed by X-ray analysis (see stereo diagram).[10]



The proton NMR spectrum of the product from preparation **3A** is much more complex and difficult to interpret. However the signal due to the H-5 axial proton is 0.2 ppm downfield when compared with the corresponding signal from the other isomer, and this effect has been seen before.[6] As the other isomer can be unequivocally identified as having structure **3B**, this isomer, prepared from 2-*O*-benzylglycerol must be and has the properties expected for structure **3A**.

Compounds **3A** and **3B** were used as model compounds to determine the lability of the dioxaphosphacyclohexane ring. Under physiological conditions both were stable, and it required 0.2 M HCl under reflux before any appreciable hydrolysis could be achieved. Under these conditions the half lives were as follows: **3A**, 2 h; **3B**, 5 h. At pH 10.6 at room temperature, the corresponding values were as follows: **3A**, 1 h; **3B**, 4 h.

Experimental Section

Synthesis of 4. Methyl phosphorodichloridate[7] (2.25 g, 15 mmol) was added to a solution of 2-*O*-benzylglycerol[8] (2.74 g, 15 mmol) and 2,6-lutidine (3.48 mL, 30 mmol) in dry benzene. After 18 h at room temperature, the mixture was filtered and the filtrate reduced to an oil which was dissolved in chloroform and fractioned on a silica column using ethanol/chloroform (5:95). The crude product was crystallized from benzene/cyclohexane (yield 1.9 g, 49%):[9] mp 66–68 °C; ^1H NMR ($CDCl_3$) δ 7.35 (5 H, s, Ph), 4.62 (2 H, s, $PhCH_2$), 4.33 (5 H, m, H-4, H-5, H-6), 3.87 (3 H, d, CH_3, J_{P-CH_3} = 12 Hz).

Synthesis of 3A. Compound **4** was debenzylated by treatment with 5% Pd/C and hydrogen in dry ethanol at atmospheric pressure and room temperature. Recrystallization of the product from toluene/petroleum ether gave the pure product (yield 45%):[9] mp 79–80 °C; ^1H NMR [$(CD_3)_2SO$] δ 5.6 (1 H, s, OH), 4.4–4.25 (2 H, m, H-4, H-6 axial), 4.02–3.9 (3 H, m, H-6, H-5, and H-4 equatorial), 3.7 (3 H, d, OCH_3, J_{P-OCH_3} = 11 Hz); ^{13}C NMR [$(CD_3)_2SO$] 71.8 (OCH_3), 61 (C_5OH), 54 (CH_2) ppm; ^{31}P NMR [$(CD_3)_2SO$] −5.1; MS, *m/e* 169, 168 (M^+), 95 (base peak), 136, 127, 110.

Synthesis of 3B. This compound was prepared exactly as described by Denney and Varga:[2] mp 111–112 °C;[9] ^1H NMR [$(CD_3)_2SO$] δ 5.6 (1 H, s, OH), 4.4 (2 H, m, H-4 and H-6 axial), 4.2 (2 H, m, H-4 and H-6 equatorial), 3.78 (1 H, m, H-5 equatorial), 3.68 (3 H, d, OCH_3, J_{P-OCH_3} = 11 Hz); ^{13}C NMR [$(CD_3)_2SO$] ppm, 73.4 (OCH_3), 62 (C_5OH), 53 (CH_2); ^{31}P NMR [$(CD_3)_2SO$] −6.8; MS, *m/e* 169, 168 (M^+), 95 (base peak), 140, 127, 110, 79.

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[9] Analytical data for the new compounds described here are in agreement with the assigned structures.

[10] The product **3B** crystals are orthorhombic, space group $Pna2_1$ with a = 10.825 Å, b = 9.342 Å, and c = 6.839 Å. The discrepancy R = 0.035 for 642 reflections.

Estimating Heats of Sublimation of Hydrocarbons. A Semiempirical Approach

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Numerous conceptual models in organic chemistry such as strain and resonance energies implicitly reference the

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Table I. Comparison of Experimental and Estimated Heats of Sublimation of Solid Hydrocarbons[a]

compound	calcd ΔH_v (from eq 1)	ΔH_{fus}[b]	calcd ΔH_s[c] (from eq 2)	exptl ΔH_s	$\frac{(\Delta H_5 - \Delta H_5{}^c)}{\Delta H_5}$
C_6					
benzene	7.4	2.4	9.8	10.6[c]	0.08
cyclohexane	7.4	0.6	8.0	8.9[d]	0.10
hexane	7.4	3.0	10.4	12.1[e]	0.14
C_8					
bicyclo[2.2.2]octene	9.7	1.3	11.0	10.5[f]	−0.05
bicyclo[2.2.2]octane	9.7	2.0	11.7	11.4[f]	−0.03
cyclooctatetraene	9.7	2.7	12.4	13.0[g]	0.05
2,2,3,3-tetramethylbutane	8.1	2.2	10.3	10.4[h]	0.01
C_{10}					
naphthalene	11.9	4.5	16.4	17.3[i]	0.05
bullvalene	11.9	3.8[bb]	15.7	17.2[j]	0.09
1,2,4,5-tetramethylbenzene	11.9	5.0	16.9	17.0[k]	0.01
tricyclo[5.2.1.0^{2,6}]decane	11.9	0.7	12.6	12.6[f]	0
C_{11}					
2-methylnaphthalene	13.0	2.9	15.9	15.7[l]	−0.01
				14.7[f]	−0.08
C_{12}					
acenaphthylene	14.2	1.7	15.9	17.4[m]	0.09
				17.0[h]	0.06
acenaphthene	14.2	4.8	19.0	19.9[n]	0.05
biphenyl	14.2	4.5	18.7	18.6[o]	−0.01
1,8-dimethylnaphthalene	14.2	3.8	18.0	19.0[n]	0.05
2,6-dimethylnaphthalene	14.2	6.0	20.2	20.2[n]	0
2,7-dimethylnaphthalene	14.2	5.6	19.8	20.0[n]	0.01
hexamethylbenzene	14.2	5.4	19.6	20.4[o]	0.04
C_{13}					
fluorene	15.3	4.8	20.1	19.9[n]	−0.01
diphenylmethane	15.3	4.4	19.7	19.7[h]	0
				15.3[d]	−0.29
				17.2[p]	−0.15
		4.6[q]	19.9	19.9[q]	0
C_{14}					
anthracene	16.4	6.9	23.3	22.5[r]	−0.04
				25.0[c]	0.07
diphenylacetylene	16.4	4.9[q]	21.3	21.5[d]	0.01
				21.6[q]	0.01
phenanthrene	16.4	4.3	20.7	22.1[c]	0.06
trans-stilbene	16.4	6.5[c]	22.9	24.8[s]	0.08
1,2-diphenylethane	16.4	5.5	21.9	21.8[s]	0
diadamantane	16.4	5.3	21.7	22.9[t]	0.05
				28.0[u]	0.22
1,2,3,4,5,6,7,8-octahydroanthracene	16.4	4.3	20.7	19.7[f]	−0.05
n-tetradecane	16.4	10.7	27.1	28.1[m]	0.04
C_{15}					
n-pentadecane	17.5	8.3	25.8	25.8[m]	0
C_{16}					
fluoranthene	18.6	4.5	23.1	23.7[f]	0.03
pyrene	18.6	4.2	22.8	23.9[v]	0.05
n-hexadecane	18.6	12.7	31.3	32.3[m]	0.03
C_{17}					
n-heptadecane	19.8	9.6	29.4	29.9[m]	0.02
C_{18}					
triphenylene	20.9	5.9	26.8	30.2[c]	0.112
				28.2[h]	0.07
				25.6[w]	−0.05
o-terphenyl	20.9	4.1	25.0	23.2[x]	−0.08
hexaethylbenzene	20.9	7.6	28.6	9.9[y]	−1.89
			28.6	22.7[q]	−0.26
n-octadecane	20.9	14.7	35.6	36.5[m]	0.02
C_{19}					
triphenylmethane	22	5.0	27.0	23.9[h]	−0.13
C_{20}					
perylene	23.1	7.6	30.7	34.7[z]	0.12
				29.9[h]	−0.03
triptycene	23.1	7.2	30.3	25.0[f]	−0.21
eicosane	23.1	14.7	37.8	40.7[m]	0.07
C_{24}					
1,3,5-triphenylbenzene	27.6	5.5	33.1	36.3[a]	0.09
				34.0[w]	0.03

[a] All units in kcal/mol. Aggrement between estimated and experimental heats of sublimation were generally within 1 kcal/mol even for compounds with less than six carbons. These compounds are not included in the table because of the uncertainties associated with polymorphism exhibited by many of them.

[b] All ΔH_{fus} values unless otherwise noted are from: Domalski, E. S.; Evans, W. H.; Hearing, E. D. *J. Phys. Chem. Ref. Data* **1984**, *13* (Supplement 1).

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gas phase. Likewise, most quantum mechanical calculations are on isolated molecules. In contrast, experimental chemistry generally deals with condensed phase species. It is therefore useful to have methods that interrelate experiment and theory by providing the energy terms between the condensed and gas phases.

Numerous successful methods have been developed for estimating heats of vaporization (ΔH_v) of liquids, particularly hydrocarbons.[1,2] However, relatively few efforts have been reported for estimating corresponding heats of sublimation (ΔH_s). One of the earliest methods reported was the development of Walden's rule[3] to estimate heats of fusion ΔH_{fus} and together with ΔH_v obtained by other methods, such as those developed by Klages[4] and Trouton,[5] an estimate of ΔH_s could be obtained. More recently a general method requiring only gross structural information has been developed by Bondi.[6] This method is based on the assumption of additivity in molecular structure increments to yield the total sublimation energy. A few other more accurate but also more restrictive relationships for some simple homologous series and for other closely related compounds have also been reported.[7]

A clear demonstration of the approximate nature of any method developed which is based on the assumption of group additivity in estimating heats of sublimation can be surmised from recent reports of the heat of sublimation and heat of fusion observed in racemic and active forms of the same chiral molecule.[8,9] Differences in the range of kilocalories/mole have been routinely observed in ΔH_{fus} (and in those ΔH_s measured) and $\Delta\Delta H_{fus}$ values as large as 5 kcal/mol have been reported.[9] In these cases the differences are clearly due to differences in molecular packing in the crystal and suggest that estimations of ΔH_{fus} or ΔH_s based on methods of group additivity are likely to remain either qualitative or restricted to members of a series which are iso structural.

The need for a reliable *albeit* qualitative method of estimating ΔH_s is particularly evident, when one consider that experimental ΔH_s values are currently available for only about 1000 simple organic solids.[10] Furthermore, even for those compounds for which data is available, the large discrepancies in reported ΔH_s often found in the literature for the same compound make it difficult for the nonspecialist and specialist alike to identify the most reliable values.

Recently, we reported a simple relationship for estimating ΔH_v of liquid hydrocarbons generally within 5% (i.e., 1 kcal/mol).[2] We would like to show that this relationship, eq 1, together with available (or easily measured) heats of fusion and the additivity of latent heats, eq 2, can give a reasonable estimate of ΔH_s. The usefulness of these two relationships, eq 1 and 2, henceforth referred to as semiempirical additivity of latent enthalpies (SEALE), as it relates to hydrocarbons is demonstrated by application.[11] In addition, estimations by the method of SEALE are compared to ΔH_s values determined by the method of indirect head space analysis and to earlier literature values for three solid hydrocarbons, diphenylacetylene, diphenylmethane, and hexaethylbenzene. The results for diphenylacetylene are representative of a case in which

$$\Delta H_v(298\ \mathrm{K}) = (0.31 \pm 0.05)n_Q + (1.12 \pm 0.02)\bar{n}_c + (0.71 \pm 0.15) \quad (1)$$

where $$\bar{n}_c = n_c - n_Q$$

$$n_c = \text{total number of carbon atoms}$$

$$n_Q = \text{number of quaternary carbon atoms}$$

$$\Delta H_s \sim \Delta H_{fus} + \Delta H_v \quad (2)$$

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(11) The approximate sign can be replaced by an equal sign for enthalpies determined at the same temperature.

estimated and experimental, both past and present, are in agreement. Diphenylmethane is a case in which estimates by the method of SEALE is useful in identifying the most reliable among several discordant literature values. The reliability of this estimation is also confirmed by experiment. Finally, hexaethylbenzene is an example of an instance in which SEALE can be useful in identifying unreliable literature values. In addition, it also focuses attention on potential limitations of this method in estimating ΔH_s.

Results and Discussion

The applicability of eq 1 and 2 in providing a reasonable estimate of ΔH_s is clearly shown in Table I. This table lists calculated heats of vaporization, ΔH_v (eq 1), experimental heats of fusion, ΔH_{fus}, and calculated (eq 2) and experimental heats of sublimation (ΔH_s^c, ΔH_s, respectively) for over 40 hydrocarbons of diverse molecular structure. The average deviation from the experimental value is ca. ±1 kcal (5%) with approximately $^2/_3$ of the calculated values slightly underestimating experimental ΔH_s. Compounds with small ΔH_s have understandably larger percentage uncertainties than those with larger ΔH_s. For those 36 compounds for which a single citation was available or when multiple citations had a total range of 1 kcal/mol or less, a linear regression analysis resulted in the equation: $\Delta H_s^c = 0.981\Delta H_s + 0.126$, $r = 0.98$, with a typical error of ca. 1-2 kcal/mol.[12] By contrast using solely the number of carbons as a predictor for the heat of sublimation of these same species resulted in the equation: $\Delta H_s^c = 1.65n_c - 0.52$, $r = 0.88$, which gave considerably poorer results.

The first entry in this table in which clearly an uncertainty exists for ΔH_s is diphenylmethane. Three discordant values have been previously reported with the most recent value (1959) in best agreement with the value estimated by SEALE. In order to confirm this result, we have repeated the ΔH_s measurement and have also measured ΔH_{fus} for diphenylmethane. Our experimental results, which are summarized in Table I, are given in Tables 1S–4S in the supplementary material (see paragraph at the end of paper about supplementary material). The calculated and measured values of 19.9 kcal/mol are in excellent agreement with results reported by Aihara.[13]

Diphenylacetylene is an example of a system which was of interest to us for a variety of reasons.[14] In this instance, however, since the experimental determination is old, having been reported in 1938,[15] we again measured both ΔH_{fus} and ΔH_s. The experimental results are reported in tables in the supplementary material (see paragraph at the end of the paper about supplementary material). Agreement in ΔH_s determined by these three independent methods is very good.

Finally, ΔH_{fus} and ΔH_s were determined for hexaethylbenzene. Even without knowledge of ΔH_{fus} for this material, it is clear that the experimental value reported in the literature[16] is too small. Our ΔH_{fus} and ΔH_s results for this material are presented in tables in the supplementary material (see paragraph at the end of paper about supplementary material). As noted in Table I, this is an example of a material in which a reasonably close estimate (<10%) is not obtained by the SEALE method. Our estimated ΔH_s of 28.5 kcal/mol compares to an experimental value of 22.7 ± 1.0 kcal/mol. We believe the reason for this discrepancy is in the limitations of eq 1. To the extent that success of eq 1 in estimating ΔH_v is related to the proportionality between the number of carbons atoms to the total effective surface area of the molecule, quarternary carbon atoms perturb this proportionality the most and thus are factored out. Hexaethylbenzene, although containing no quarternary carbons, is nevertheless congested and it is likely that the effective surface area for such a molecule is less than that for the other C_{18} hydrocarbons reported in Table I. The implications of these results and those in Table I are that estimates by the method of SEALE, as presently described by eq 1, are apt to be slightly lower than experimental ΔH_s for planar and linear hydrocarbons and larger than experimental values for conjested hydrocarbons which do not contain quarternary carbon atoms. Prominent examples of hydrocarbons in which estimated ΔH_s values are overestimated by more than 5% of the reported value in Table I include bicyclo[2.2.2]octene, 1,2,3,4,5,6,7,8-octahydroanthracene, *o*-terphenyl, triphenylmethane, and triptycene, molecules whose effective Van der Waals surface area might be less than suggested solely by carbon number. Bullvalene is the only example of a molecule of similar structure which is underestimated by eq 1 and 2 by more than 5%. Further refinement of eq 1 is likely but must await additional experimental data.

Experimental Section

Diphenylacetylene (99%, mp 59–61 °C) and diphenylmethane (Gold Label 99+%) were obtained from Aldrich Chemical Co. and used without further purification. Hexaethylbenzene, obtained from Eastman Kodak Co., was recrystallized twice from ethyl acetate and sublimed (mp 128 °C) before use.

Heats of fusion were measured on a Perkin-Elmer DSC-2 differential scanning calorimeter. The area under the curves was determined by duplicate analysis by the cut and weight technique and results were reproducible to 2%. Heats of fusion were calculated on the basis of five determinations for each substance reported. Indium was used as the standard for calibration. A value of 6.8 cal/g was used in the calculations.

Heats of sublimation were measured by the method of indirect head space analysis. The technique and apparatus has been described in detail elsewhere.[10] A period of 500 s was used for sample equilibration and 400 s for sample collection. Analysis of the amount of sample collected (see paragraph at the end of the paper about supplementary material) was achieved by using ultraviolet spectroscopy. All compounds obeyed the Beer–Lambert law under the conditions used. Ultraviolet spectra for diphenylacetylene (λ_{max} 2760 Å; log ϵ, 4.48; methanol) were recorded on a Beckman Acta MVI spectrophotometer while ultraviolet spectra for hexaethylbenzene (λ_{max} 2720 Å; log ϵ, 5.22; cyclohexane) and diphenylmethane (λ_{max}, 2700 Å; log ϵ, 5.58; absolute alcohol) were recorded on a Cary 14 spectrophotometer.

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Supplementary Material Available: Full vapor pressure data for diphenylmethane, diphenylacetylene, and hexaethylbenzene (4 pages). Ordering information is given on any current masthead page.

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(12) It is hard to compare our method with those discussed in the literature (ref 1, 6) because these latter methods are either highly specialized (e.g., to only alkanes) or highly parametrized. Nonetheless, our current approach maintains the complementary virtues of simplicity and accuracy demonstrated eariler in ref 2.

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