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Note

Heat of solution in a polyethylene glycol stationary phase of several cyclic and bicyclic compounds

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In previous papers^{1,2} we reported studies of the heat of solution (ΔH_s) for several acyclic hydrocarbons, aldehydes, esters and alcohols in non-polar (squalane) and polar (Carbowax 20M) stationary phases. It was found that ΔH_s was dependent on the polarity of the functional group. Thus, decreasing in the order alcohols > carbonyls > hydrocarbons. On the other hand, $\Delta(\Delta H_s)$ for an acyclic CH_2 group is 3.3 ± 0.8 kJ/mol, independent of the chemical function present in the compound.

This paper reports ΔH_s values for some bicycloketones (6 and 9), spirolactones (5, 7 and 8) and unsaturated hydroxy esters with a cyclic substituent (1, 2, 3 and 4) that were prepared by a method described previously³ (Scheme 1). The heat of solution was calculated in order to study the behaviour of different cyclic systems with respect to ΔH_s and the influence of the different compounds on the values of ΔH_s and $\Delta(\Delta H_s)$ for a cyclic CH_2 group.

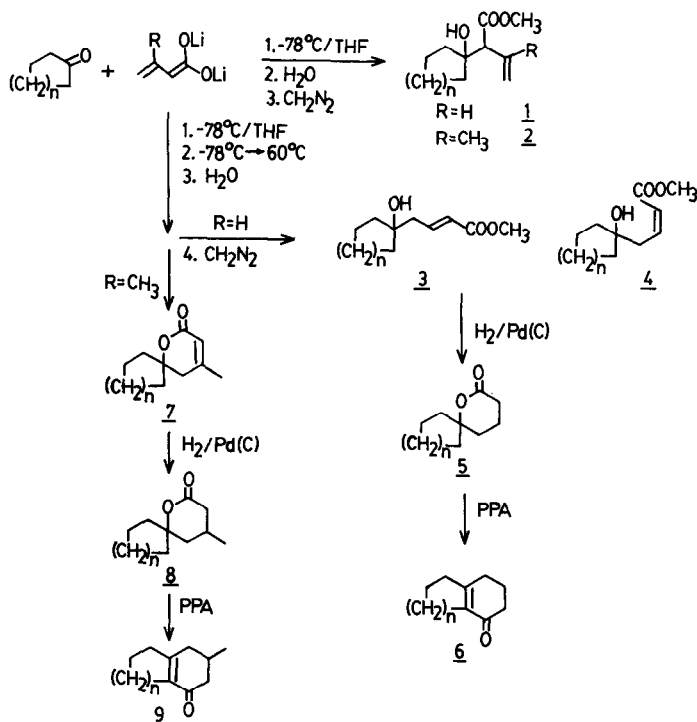
EXPERIMENTAL

The ΔH_s values were calculated from the slopes of plots of $\ln(V_R^0/T)$ vs. $1/T$, where V_R^0 , the corrected retention volume, is

$$V_R^0 = t_R^* \varphi$$

t_R^* is the corrected retention time (min), φ is the flow-rate of the carrier gas (ml/min) and ΔH_s represents the sum of $\Delta H(\text{solution})$ and $\Delta H(\text{vaporization})$.

Retention times were determined with a Hewlett-Packard Model 5834A chromatograph equipped with a Model 18850A integrator and a flame ionization detector. A stainless-steel column (2 m \times 1/4 in. I.D.) packed with Carbowax 20M (polyethylene glycol, MW \approx 20 000) and nitroterephthalic acid ester (free fatty acid phase, FFAP) on Chromosorb P AW DMCS (60-80 mesh), supplied by Teknokroma (Barcelona, Spain), was used. Nitrogen was used as the carrier gas at a flow-rate of 37 ml/min. The determinations were carried out at 220, 230 and 240°C with the injector and flame ionization detector operating at 250°C. Compounds were injected (0.3 μ l) as solutions in diethyl ether (3%, w/w). Retention times were measured from the time of sample injection. The dead volume was determined by regression analysis on a series of *n*-alkanes (C_{10} - C_{24}) using the Grobler and Bálsiz procedure⁴.



Scheme 1.

TABLE I
 ΔH_s VALUES (kJ/mol) FOR THE COMPOUNDS STUDIED

<i>n</i>	Compound type								
	1*	2*	3	4**	5	6	7	8	9
1	-41.4	-46.4	-55.6	-53.9	-43.5	-41.4	-68.1	-48.5	-42.6
2	-45.6	-50.2	-59.8	-57.7	-46.8	-44.3	-71.5	-51.8	-45.1
3	-50.2	-53.9	-63.9	-62.3	-50.2	-46.8	-76.1	-55.2	-48.1
4	-53.9	—	-68.1	—	-54.3	-50.2	-79.8	-58.9	-51.4
6	—	—	-76.1	—	-60.2	-55.6	-87.4	-64.8	-56.8
8	-70.6	—	-84.0	-81.9	-66.0	-61.0	-94.9	-71.1	-62.3
$\Delta(\Delta H_s)$	-3.7	-3.8	-4.0	-4.0	-3.2	-2.8	-3.8	-3.2	-2.8
s^{***}	0.50	—	0.18	0.29	0.50	0.21	0.29	0.33	0.25

* Compounds 1 and 2 are very labile substances and most of them decompose totally or partially under chromatographic conditions.

** Compounds 4 are not generally isolated. Retention times were calculated from crude mixtures.

*** Standard deviation.

RESULTS AND DISCUSSION

The ΔH_s values of the compounds studied are given in Table I. In all instances, plots of ΔH_s vs. number of cyclic CH_2 groups (n) (see Scheme 1) yield straight lines with high accuracy and low standard deviations (Fig. 1). We consider that the solute-stationary phase interactions depend principally on a number of "active groups" present in the molecule. The "active group" may be described as "the functional group that produces an interaction with the stationary phase more efficiently than an alkane"; for example, see Scheme 2, where a lactone and a double bond would be "active groups".

Compounds 1, 3 and 4 in Scheme 3 have the same number of "active groups" (COOCH_3 , OH and $\text{CH}=\text{CH}$) and hence the different values of ΔH_s will be direct

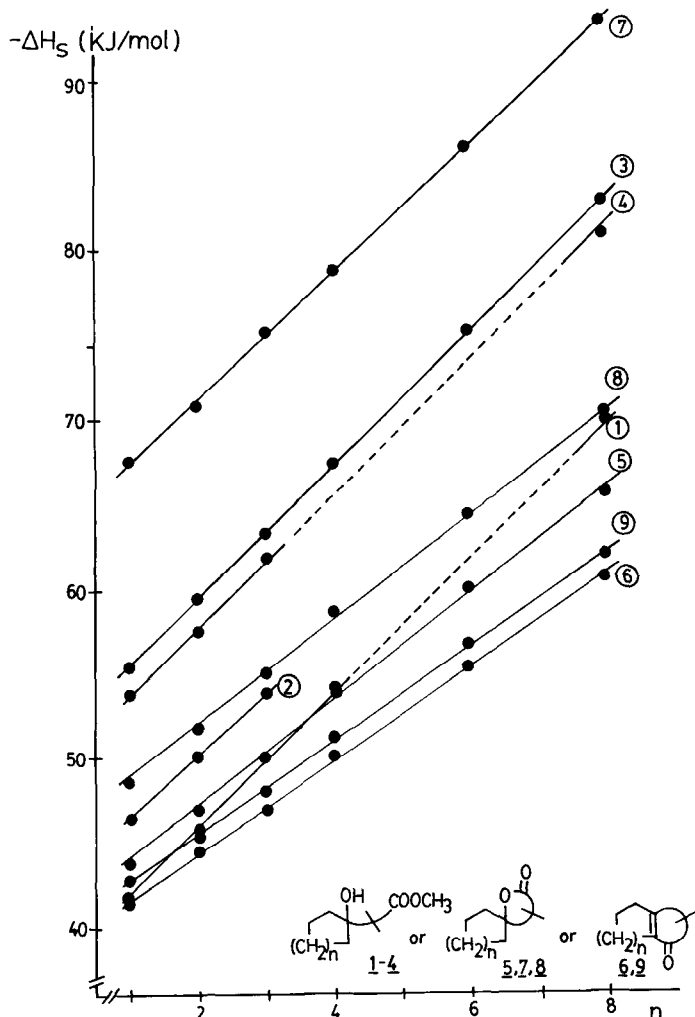
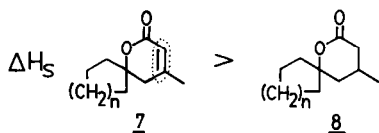
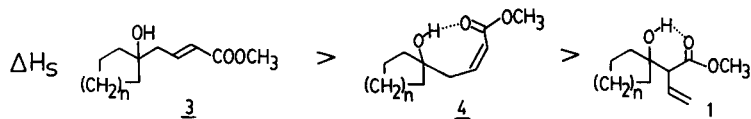


Fig. 1. ΔH_s (kJ/mol) vs. n for the compounds studied. The numbers on the lines are the compound types (see text).



Scheme 2.



Scheme 3.

functions of the higher or lower molecular interactions between these “active functions”, that is, the higher the internal interactions the lower is ΔH_s .

For example, the methyl 4-(1-hydroxy-1-cycloalkyl)-2-(*E*)-butenoates (3) cannot undergo any intramolecular interactions, whereas the corresponding (*Z*)-butenoates (4) can show a slight interaction-type hydrogen bond, although an eight-membered ring is unstable. However, the corresponding methyl 2-(hydroxy-1-cycloalkyl)-3-butenoates (1) can form a stable six-membered ring by hydrogen bonding and therefore ΔH_s decreases. A similar behaviour is shown by spirolactones, where an increase in ΔH_s for 7 vs. 8 is produced, owing to the additional double bond in 7 (see Scheme 2).

Although the number of “active groups” is an important parameter determining the sequence of ΔH_s values for closely related compounds, the conformational rigidity of the organic structure can enhance or diminish the ΔH_s values. Thus, the spirolactones (7) show the highest values for the compounds studied and the bicycloalkanones (6) show the lowest values.

On the other hand, in all instances, the ΔH_s value for a cyclic CH_2 group is almost constant at -3.3 ± 0.8 kJ/mol (see Table I), independent of the type of structure. This value is similar to that for the acyclic systems previously reported². The approximate constancy of $\Delta(\Delta H_s)$ for a CH_2 group implies zero excess enthalpies, or at least values no greater than 0–800 J/mol, which would be too small to affect ΔH_s . We conclude that the ΔH_s values are equivalent to enthalpies of condensation (vaporization).

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