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CONFORMATIONS OF PENTAN-1-OL, HEXAN-1-OL AND THEIR THIO ANALOGUES

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Empirical linear relationships between standard Gibbs free energy, ΔG°_{298}, and parachor and between standard entropy, S°_{298}, and parachor are presented for the aliphatic series $H(CH_2)_nX$ with X = CH_3, $CH=CH_2$, $C\equiv CH$, Cl, OH, SH, SCH_3 and SC_2H_5. In the series with X = OH and SH significant deviations of points for $n = 4$ and 5 are observed. INDO quantum-chemical analysis points to the formation of cyclic conformers of butan-1-ol, pentan-1-ol and their corresponding thio analogues. The formation energy of the cyclic conformers (higher for thiols than for alcohols) is proportional to the sum of deviations from the linearity of the points under discussion.

INTRODUCTION

Either the state functions or parachors of molecules are available based on the additivity principle from the energies or parachors, respectively, of all the individual atoms and bonds.[1–4] Hence one may expect linearity between thermodynamic functions and molecular parachor within homologous series. Indeed, such linearity was reported between standard enthalpy, ΔH°_{298}, and molecular parachor for a number of aliphatic series, $H(CH_2)_nX$, where X is various substituents.[5] Attempts to study similar relationships between the standard Gibbs free energy, ΔG°_{298}, and standard entropy, S°_{298}, and parachor have revealed some deviations of the points for $n = 4$ and 5 in each of eight series studied.

In this paper, the reasons for the deviations of points for $n = 4$ and 5 in aliphatic series $H(CH_2)_nX$, particularly notable when X = OH, SH and S-alkyl, are interpreted in terms of changes in conformations.

STANDARD FREE ENERGY AND STANDARD ENTROPY – MOLECULAR PARACHOR CORRELATIONS

Standard Gibbs free energies of formation in the gas phase, ΔG°_{298} (in kcal mol^{-1}; 1 kcal = 4·184 kJ), and standard entropies, S°_{298} (in cal K^{-1} mol^{-1}, were taken from available catalogues.[6,7] The parameters and the quality of regressions

$$\Delta G^\circ_{298} = \xi P + \nu \quad (1)$$

$$S^\circ_{298} = \xi P + \nu \quad (2)$$

for eight series tested are given in Table 1 (for ΔG°_{298}) and 2 (for S°_{298}).

The slopes for both equations (1) and (2) are virtually insensitive for X. They are low and all around 0.05 in equation (1) and 0.24 in equation (2). A similar lack of sensitivity of ξ to X was observed for regressions of ΔH°_{298} vs P ($\xi = -0.13$).[5] In contrast, ν varies from one series to another.

The lowest correlation coefficients were calculated for the series of alcohols and thiols: Table 3 reports the

Table 1. Parameters and quality of the correlation equation $\Delta G^\circ_{298} = \xi P + \nu$ in the aliphatic series, $H(CH_2)_nX$[a]

X	ξ[b]	ν[c]	n[d]	r[e]	s[f]
CH_3	0·0506	−13·5492	10	0·999784	0·132
$CH=CH_2$	0·0512	7·8192	10	0·999978	0·043
$C\equiv CH$	0·0511	39·6321	10	0·999970	0·050
Cl	0·0375	−19·2002	5	0·989535	0·390
OH	0·0444	−45·7402	10	0·972045	1·342
SH	0·0498	−18·6402	10	0·998337	0·361
SCH_3	0·0492	−16·5153	10	0·998486	0·340
SC_2H_5	0·0492	−17·1796	10	0·998838	0·298

[a] Based on data in the gas phase.
[b] Slope of regression.
[c] Intercept.
[d] Number of experimental points.
[e] Correlation coefficient.
[f] Standard deviation.

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Table 2. Parameters and quality of the correlation equation $S^{\circ}_{298} = \xi P + \nu$ in the aliphatic series, $H(CH_2)_nX$[a]

X	ξ	ν	n	r	s
CH_3	0·2407	28·1540	10	0·999985	0·162
$CH{=}CH_2$	0·2393	30·3175	10	0·999996	0·087
$C{\equiv}CH$	0·2399	28·8431	10	0·999963	0·259
Cl	0·2519	28·2717	5	0·999788	0·370
OH	0·2406	36·2276	10	0·999367	1·073
SH	0·2412	32·0757	10	0·999978	0·200
SCH_3	0·2422	30·7845	10	0·999820	0·576
SC_2H_5	0·2416	31·4358	10	0·999878	0·473

[a] See footnotes a–f in Table 1.

Table 3. Deviations, $\delta(\Delta G^{\circ}_{298})$ and δS°_{298}, of the points from the linear relationships in the series of alcohols and thiols[a]

	$H(CH_2)_nOH$			$H(CH_2)_nSH$		
n	P	$\delta(\Delta G^{\circ}_{298})$	δS°_{298}	P	$\delta(\Delta G^{\circ}_{298})$	δS°_{298}
2	132·2	−0·3955	−0·4579	160·4	−0·0156	0·0069
3	171·2	−1·1759	0·2078	199·4	−0·3197	0·2304
4	210·2	−1·7064	2·6135	238·4	−0·1438	0·1038
5	249·2	−0·7168	0·0192	277·4	−0·6179	0·0673
6	288·2	−0·3772	−0·0552	316·4	−0·0421	0·1907
7	327·2	−0·0676	−0·1295	355·4	0·0238	0·0942
8	366·2	0·2219	−0·2038	394·4	0·0797	−0·0024
9	405·2	0·5215	−0·2781	433·4	0·1456	−0·0989
10	444·2	0·8111	−0·3524	472·4	0·2115	−0·1955

[a] The magnitudes are given in the following units: P, cm^3(10^{-3}N m$^{-1,1/4}$; $\delta(\Delta G^{\circ}_{298})$, kcal mol^{-1}; δS°_{298}, cal K^{-1} mol^{-1}.

Table 4. Relative deviations, $\delta(\Delta G^{\circ,\mathrm{I}}_{298})$ and $\delta S^{\circ,\mathrm{I}}_{298}$, for the compounds with $n = 4$ and 5[a]

	$H(CH_2)_nOH$		$H(CH_2)_nSH$	
n	$\delta(\Delta G^{\circ,\mathrm{I}}_{298})$	$T\delta S^{\circ,\mathrm{I}}_{298}$	$\delta(\Delta G^{\circ,\mathrm{I}}_{298})$	$T\delta S^{\circ,\mathrm{I}}_{298}$
2	0·0000	0·0000	0·0000	0·0000
4	−1·3109	0·9153	−0·1282	0·0288
5	−0·3213	0·1422	−0·6023	0·0180

[a] Values in kcal mol^{-1}; $T = 298$ K.

deviations, δ, between calculated and regressed points for the two series.

Deviations of $\delta(\Delta G_{298})$ and δS°_{298} for butan-1-ol and $\delta(\Delta G^{\circ}_{298})$ for pentane-1-thiol are the most significant. In order to establish more exactly the ability of alcohols and thiols with $n = 4$ and 5 to form cyclic conformations of lower energy, it would be beneficial to subtract from $\delta(\Delta G^{\circ}_{298})$ and δS°_{298} some side-effects residing in these data. The values of $\delta(\Delta G^{\circ}_{298})$ and δS°_{298} for ethanol and ethanethiol ($n = 2$), which obviously cannot exist in cyclic conformations, seem to be rough measures of these effects. In this manner, relative deviations $\delta(\Delta G^{\circ,\mathrm{I}}_{298})$ and $\Delta S^{\circ,\mathrm{I}}_{298}$ were derived and are given in Table 4.

The difference between the energies of the open-chain conformers (E_A) and cyclic conformers (E_B), ΔE_{AB}, should be proportional to $\delta(\Delta G^{\circ,\mathrm{I}}_{298}) + T\delta S^{\circ,\mathrm{I}}_{298}$:

$$\Delta E_{AB} = E_B - E_A = a[\delta(\Delta G^{\circ,\mathrm{I}}_{298}) + b\delta S^{\circ,\mathrm{I}}_{298}) \qquad (3)$$

where a and b are constants. The constant b, which is close to but different from 1, normalizes the $T\delta S^{\circ,\mathrm{I}}_{298}$ term to $\Delta(\Delta G^{\circ,\mathrm{I}}_{298})$, as both deviations originate from two different regressions. Both a and b are available from the quantum-chemical analysis of energies of particular conformers, E_A and E_B.

QUANTUM-CHEMICAL CALCULATIONS

The INDO method with the Boehm and Gleiter parameterization[8] was involved in the calculations for the closed-shell system of the molecules in their ground states. Additionally, a previously described modification[9] was introduced into the method applied: in the Boehm–Gleiter formalism of the core electron, the V^{AA}_{B} integral $\alpha = 0.70$ and $f^1 = 1.0$ was used if the Ath atom is hydrogen. This modification leads to a small penetration effect on the 1s hydrogen atomic orbital. In this manner the energies of the molecular orbitals are improved with respect to those available by the *ab initio* method. Standard geometry was taken into consideration with bond lengths and bond angles as in Table 5.

The calculations of energies E_A and E_B, molecular orbital energies and coefficients of eigenvectors were carried out for conformers of butan-1-ol, pentan-1-ol, butane-1-thiol and pentane-1-thiol with the valence sp basis of atomic orbital involved.

Table 5. Bond lengths and angles taken into consideration

Bond	Length (Å)	Angle (°)	Ref.
C(sp^3)—C(sp^3)	1·534		10
C(sp^3)—H	1·093		10
C(sp^3)—O	1·480		11
O—H	0·951		11
C(sp^3)—S	1·810		12
S—H	1·352		12
CCC, CCH, HCH[a]		109° 28′	10

[a] All values involve C(sp^3) carbon atoms.

RESULTS AND DISCUSSION

The possibility of each of butan-1-ol, butane-1-thiol, pentan-1-ol and pentane-1-thiol taking two conformations was assumed. Thus, they may take either an open-chain conformation (A) or a cyclic conformation (B). Cyclic conformations are shown in Figures 1–3.

Total energies (E_A and E_B) of the conformers of these molecules are given in Table 6. The energies of the formation of the cyclic conformations are hence available and they are quoted in Table 7 in form of the contributions from electronic and repulsion components to the overall energy of the formation of the ring. These values allowed the calculation for equation (3) of $a = 1000$ and $b = 1.4193$. These calculations were carried out under assumption that

$$\sum_i |\Delta E_{AB_i} - \Delta E_{AB_i}^{INDO}| = \min \qquad (4)$$

where $i = C_4H_9OH$, $C_5H_{11}OH$, C_4H_9SH and $C_5H_{11}SH$, ΔE_{AB_i} is calculated from simple regressions according to equation (3) and $\Delta E_{AB_i}^{INDO}$ are heats of formation of cyclic conformations according to INDO.

Comparison of theoretical values of ΔE_{AB} of quantum-chemical origin with those obtained from equation (3) showed satisfactory agreement for all four compounds under consideration. This agreement gives

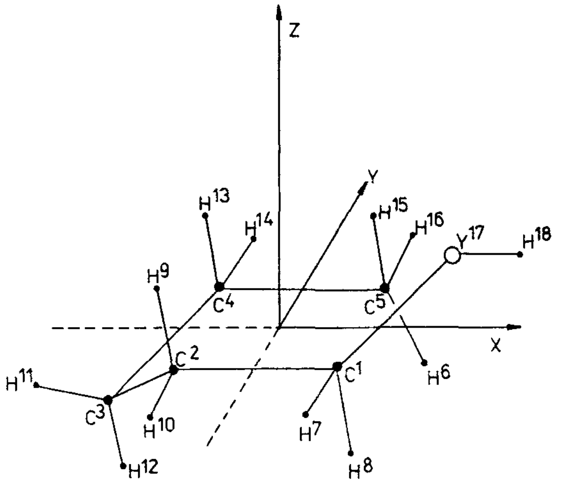


Figure 2. Chair-like cyclic conformations of pentan-1-ol ($Y^{17} = O^{17}$) and pentane-1-thiol ($Y^{17} = S^{17}$)

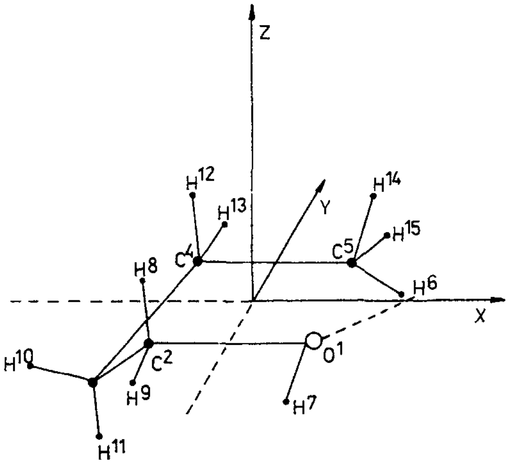


Figure 1. Structure of the cyclic conformer of butan-1-ol

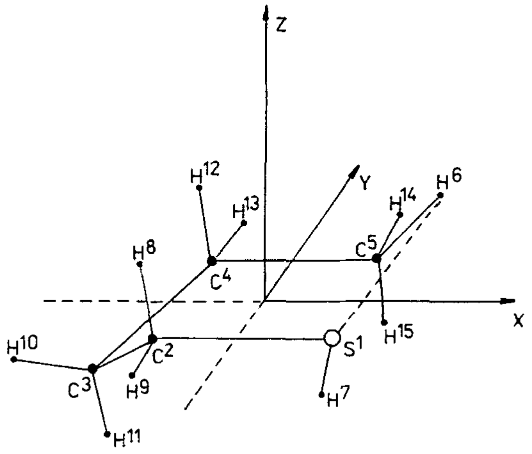


Figure 3. Chair-like cyclic conformation of butane-1-thiol

Table 6. Energies of the conformations and corresponding heats of formation of the cyclic conformers for alcohols and thiols with $n = 4$ and 5

Compound	Energy of conformer: Open-chain, E_A (eV)	Cyclic, E_B (eV)	ΔE_{AB}^{INDO} (kcal mol^{-1})	Heat of formation, $E_B - E_A$ (kcal mol^{-1}) [calculated from equation (3)]
C_4H_9OH	−1364·7837	−1365·4809	−16·079	−11·8
$C_5H_{11}OH$	−1591·4912	−1598·5219	−162·149	−119·5
C_4H_9SH	−1296·3622	−1300·4808	−94·987	−87·3
$C_5H_{11}SH$	−1522·0245	−1542·1960	−465·215	−576·7

evidence that cyclization into B conformers is the reason for the deviations observed for the members with $n = 4$ and 5 in the aliphatic series (see Table 6).

The formation of the cyclic conformer of butan-1-ol is weakly exothermic ($-16\ \mathrm{kcal\,mol^{-1}}$), in spite of high deviations in ΔG°_{298} and S°_{298}, whereas the cyclization of butane-1-thiol into its cyclic conformer is strongly exothermic ($-95\ \mathrm{kcal\,mol^{-1}}$) in spite of low deviations in ΔG°_{298} and S°_{298} (see Table 4). The total energy of ring formation is the sum of electronic and repulsion energies:

$$\Delta E_{\mathrm{AB}} = \Delta E^{\mathrm{el}}_{\mathrm{AB}} + \Delta E^{\mathrm{rep}}_{\mathrm{AB}} \tag{5}$$

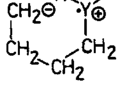
where $\Delta E^{\mathrm{el}}_{\mathrm{AB}} = E^{\mathrm{el}}_{\mathrm{B}} - E^{\mathrm{el}}_{\mathrm{A}}$ and $\Delta E^{\mathrm{rep}}_{\mathrm{AB}} = E^{\mathrm{rep}}_{\mathrm{B}} - E^{\mathrm{rep}}_{\mathrm{A}}$.

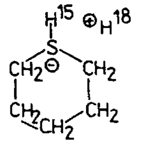
Inspection of Table 7 shows that alcohols have a greater electronic ability than thiols to form cyclic conformers. On the other hand, the bond distances in thiols are longer than those in alcohols. This factor decreases considerably the $\Delta E^{\mathrm{rep}}_{\mathrm{AB}}$ values of thiols in comparison with the corresponding values for butan-1-ol and pentan-1-ol. Hence the energy of formation of six-membered cyclic conformers is higher than the corresponding energy of formation of five-membered conformers.

Table 7. Electronic and repulsion components of the total energy of formation of the cyclic conformers of butan-1-ol, pentan-1-ol and their thio analogues

Compound	$E^{\mathrm{el}}_{\mathrm{B}} - E^{\mathrm{el}}_{\mathrm{A}}$ (eV)	$E^{\mathrm{rep}}_{\mathrm{B}} - E^{\mathrm{rep}}_{\mathrm{A}}$ (eV)
C_4H_9OH	−233·1424	232·4452
C_4H_9SH	−174·2384	170·1199
$C_5H_{11}OH$	−520·9596	513·9289
$C_5H_{11}SH$	−468·0290	477·8575

The structures of HOMO and NHOMO are given in Table 8. These data help to reveal the role of the bonding forces in the cyclic conformers. Both butan-1-ol and butane-1-thiol in such conformations have similar structures of HOMO (see also Figures 1 and 3). Because of the antibonding contributions, $\sigma^*(O^1\text{—}H^6)^{1.22}$ and $\sigma^*(S^1\text{—}H^6)^{1.28}$, both conformers are rather unstable. On the other hand, the structures of HOMO indicate that if both molecules are excited and are ionized by electron transfer from HOMO, conformers with an ionic character (**1**) may be achieved,


(1)


(2)

where Y = O, S. These correspond to the structures met in the McLafferty rearrangement.[13]

The structures of NHOMO of pentan-1-ol and pentane-1-thiol also resemble one another, and indicate the formation of $C^5\text{—}O^{17}$ and $C^5\text{—}S^{17}$ bonds, respectively, which are responsible for closing of the cyclic conformations (see also Figure 2). The electron densities on all C^5, H^{15}, H^{18} and O^{17} or S^{17} atoms are given in Table 9.

The highly positive charge density at C^5 (*ca* +0.7 a.u.) makes this atom a strong electron acceptor

Table 8. Characteristics of HOMO and NHOMO of the (A) open-chain and (B) cyclic conformers of butan-1-ol, pentan-1-ol and their thio analogues[a]

Compound		MO	Energy (eV)	Contribution of atoms to the MO's electron pair	Nonbonding, bonding and antibonding electron configuration
C_4H_9OH	(A)	HO	−12·0767	81% O^1	$n(O^1)^{1\cdot62}$
	(B)	HO	−8·9134	47·1% O^1, 30·5% C^5, 14·2% H^6	$\sigma^*(O^1\text{—}H^6)^{1\cdot22}$, $\sigma(C^5\text{—}H^6)^{0\cdot89}$
		NHO	−12·5788	78·9% O^1	$n(O^1)^{1\cdot58}$
$C_5H_{11}OH$	(A)	HO	−12·0313	82·4% O^1	$n(O^1)^{1.64}$
	(B)	HO	−7·2245	32·8% O^{17}, 28·5% H^6, 20·0% H^{15}	$\sigma^*(H^6\text{—}O^{17}\text{—}H^{15})^{1\cdot62}$
		NHO	−11·5602	46·2% O^{17}, 21·3% C^5, 10·3% H^6	$\sigma(H^6\text{—}C^5\text{—}O^{17})^{1\cdot50}$
C_4H_9SH	(A)	HO	−14·5853	21·6% C^9, 15·3% H^{11}, 15·3% H^{12}	$\sigma(H^{11}\text{—}C^9\text{—}H^{12})^{1\cdot04}$
	(B)	HO	−11·9255	39·4% S^1, 24·9% H^6, 20·5% C^5	$\sigma^*(S^1\text{—}H^6)^{1.28}$, $\sigma(C^5\text{—}H^6)^{0\cdot90}$
		NHO	−14·5751	20·3% C^4, 17·6% C^5, 17·0% H^{15}	$\sigma(C^5\text{—}H^{15})^{0\cdot69}$, $\sigma(C^4\text{—}H^{12})^{0\cdot74}$
$C_5H_{11}SH$	(A)	HO	−14·3580	22·3% C^9, 19·6% C^{13}, 19·3% C^{10}	$\sigma(C^4\text{—}C^9\text{—}C^{10}\text{—}C^{13})^{1\cdot26}$
	(B)	HO	−10·1136	36% S^{17}, 25·6% H^{15}, 17·3% H^{18}	$\sigma^*(H^{15}\text{—}S^{17}\text{—}H^{18})^{1\cdot58}$
		NHO	−14·0887	19·5% H^6, 17·1% C^5, 14·0% S^{17}	$\sigma(H^6\text{—}C^5\text{—}S^{17})^{1\cdot01}$

[a] The numbering of atoms in the cyclic conformers is presented in Figures 1–3, and that in the open-chain conformers is as follows (Y = O, S):

$$H^{13}\text{——}\underset{10}{\overset{H^{14}H^{15}}{C}}\text{——}\underset{9}{\overset{H^{11}H^{12}}{C}}\text{——}\underset{4}{\overset{H^{8}H^{7}}{C}}\text{——}\underset{3}{\overset{H^{5}H^{6}}{C}}\text{——}\underset{1}{Y}\text{——}\underset{2}{H};\ H^{16}\text{——}\underset{13}{\overset{H^{17}H^{18}}{C}}\text{——}\underset{10}{\overset{H^{15}H^{14}}{C}}\text{——}\underset{9}{\overset{H^{12}H^{11}}{C}}\text{——}\underset{4}{\overset{H^{8}H^{7}}{C}}\text{——}\underset{3}{\overset{H^{5}H^{6}}{C}}\text{——}\underset{1}{Y}\text{——}\underset{2}{H}$$

Table 9. Electronic densities on selected atoms of conformers of pentan-1-ol and pentane-1-thiol

		Atomic centres[a]			
		C^{10}	H^{12}	$O^1(S^1)$	H^2
Compound	Conformer	C^5	H^{15}	$O^{17}(S^{17})$	H^{18}
Pentan-1-ol	Open-chain	3·812	1·044	6·282	0·839
	Cyclic	3·343	1·272	5·986	0·920
Pentane-1-thiol	Open-chain	3·813	1·040	6·641	0·685
	Cyclic	3·306	1·277	6·567	0·891

[a] Top row, notation for open-chain conformers; bottom row, notation for cyclic conformers.

in both cyclic B conformers, whereas both the O^{17} and S^{17} atoms are electron donors. Hence, both C^5—O^{17} and S^{17}—C^5 bonds have considerable donor–acceptor interactions, even stronger than those in charge-transfer complexes.[14] The charge density of 0.27–0.28 electron is accumulated on the H^{15} atom in both conformers of $n = 5$. Hence the H^{15} atom takes the role of the electron donor. Moreover, the electron on H^{18} increases by *ca* 0.081 and 0.206 electron in pentan-1-ol and pentane-1-thiol, respectively. The formation of the cyclic B conformer of pentan-1-ol yields $-162\ \mathrm{kcal\,mol^{-1}}$ whereas that formation of same conformer of pentane-1-thiol yields $-465\ \mathrm{kcal\,mol^{-1}}$. This high value for the formation of the cyclic conformer of pentane-1-thiol perhaps results from apparently too low a ΔE_{AB}^{rep} component.

The analysis of the structures of both cyclic conformers for $n = 5$ suggests the formation of O^{17}—H^{15} and S^{17}—H^{15} bonds, respectively, as a consequence of the ionization from HOMO. The ionized pentane-1-thiol might take the structure **2**, the formation of which is documented in the fragmentation of ethers.

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