

Heats of Formation and Conformational Energies of 1,3-Dioxane and Its Methyl Homologues

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Heats of formation, ΔH_f° (liq.), of four methyl-substituted 1,3-dioxanes were determined by measuring their heats of combustion, ΔH_c° (liq.), at 25.0°C. The group increments of methyl substituents at different positions were evaluated from the determined heats of formation, and the conformational energies of axial methyl groups at different positions were estimated. Moreover, the enthalpy difference between the chair and skew-boat forms of the 1,3-dioxane ring was found to be slightly higher than that between the corresponding forms of cyclohexane.

Very little attention has been hitherto paid to the heats of formation of 1,3-dioxane and its methyl homologues. Some combustion data for these compounds were recently presented by Pihlaja and Heikkilä,^{1,2} who estimated some group increments¹ and conformational energies² in the gaseous state at 25°C and discussed earlier results. It was of interest to study the combustion of other methyl-substituted 1,3-dioxanes and to calculate the group increments and conformational energies of the methyl groups from the heats of formation.

EXPERIMENTAL

4,4,6-Trimethyl-1,3-dioxane was prepared by the method of Rondestvedt³ from paraformaldehyde and 2-methyl-2,4-pentanediol. Physical constants:^{4,5} b.p. 143.2°C, d_4^{20} 0.9296, n_D^{20} 1.4208; $(R_D)_{\text{obs}}$ 30.83 (calc. 30.90). Purity $\geq 99.99\%$.

4,6-Dimethyl-1,3-dioxane was prepared by the same method from paraformaldehyde and a mixture of the *meso* and DL forms of 2,4-pentanediol. The product contained two isomers of which the more volatile form had the *cis* and the less volatile the *trans* configuration.^{4,5} Physical constants:

cis-4,6-Dimethyl-1,3-dioxane: b.p. 126.6°C, d_4^{20} 0.9331, n_D^{20} 1.4136; $(R_D)_{\text{obs}}$ 31.08 (calc. 30.90). Purity $\geq 99.99\%$.

trans-4,6-Dimethyl-1,3-dioxane: b.p. 137.0–137.2°C, d_4^{20} 0.9621, n_D^{20} 1.4186; $(R_D)_{\text{obs}}$ 30.72 (calc. 30.90). Purity $\geq 99.99\%$.

2,2-Dimethyl-1,3-dioxane was prepared by the method of Böeseken and Hermans⁶ from acetone and 1,3-propanediol. Physical constants:^{6,8} b.p. 125.0–125.5°C, d_4^{20} 0.9592, n_D^{20} 1.4207; $(R_D)_{\text{obs}}$ 30.69 (calc. 30.90). Purity $\geq 99.99\%$.

Calorimetric measurements: The cyclic acetals were burned in oxygen in an adiabatic bomb calorimeter No. 1221 manufactured by Parr Instruments Co., Illinois, U.S.A. The calorimeter was equipped with No. 1101 double valve bomb and with No. 1601 standard thermometers. The internal volume of the bomb was 0.3605 l and before each experiment 1.00 g of water was added in the bomb. In each combustion experiment the bomb was charged with oxygen to an initial pressure of 30 atm. at 25°C.

The energy equivalent e° (calor) of the standard calorimeter system which contained all but the sample was determined by burning Parr standard benzoic acid pellets ($-\Delta E_B/M = 6317.83 \pm 0.62$ cal/g) and corrections to the standardized calibration conditions were made when necessary.⁷ In addition recalibrations were carried out following any change (e.g. replacement of crucible) in the calorimeter system.

Most of the samples burnt were sealed in Parr gelatin capsules, but the isomeric 4,6-dimethyl-1,3-dioxanes were combusted in glass ampoules and gelatin capsules in order to compare the results (Table 2). Owing to the hygroscopic nature of gelatin the weighing and filling of the capsules was carried out as soon as possible and similarly in every case. Thus the capsules were in air not more than ten minutes. The samples were fired at $25.00 \pm 0.02^\circ\text{C}$ using an amount of substance sufficient to bring about an increase of approximately 3.6°F (2°C) in the calorimeter temperature.

Only those combustions after which no carbon deposits were seen in the bomb were accepted as yielding reliable results. The water contents of the reagents were minimized by several distillations on sodium, the last distillation having taken place immediately before the combustion.

The corrections for nitric acid formation (from traces of nitrogen in the oxygen) were based on 14074 cal/mole at 25°C for the energy of formation of 0.1 N nitric acid from N_2 , O_2 and water.⁸ The corrections for sulfuric acid formation (from the sulfur in gelatin) were based on 72000 cal/mole at 25°C for the energy of formation of 0.17 N sulfuric acid.

The corrections for the loss in weight of the igniting wire coil (initial weight ab. 16 mg) were based on the value 1.4 cal/mg.

The corrections for the energy of combustion of the gelatin capsules were determined from the measurements of the heat of combustion of random samples chosen from a given lot of 100 capsules. The gelatin contained $0.35 \pm 0.05\%$ of sulfur and approximately 47.4 % of carbon, 17.1 % of nitrogen, 28.3 % of oxygen and 6.9 % of hydrogen. The combustion experiments with gelatin capsules are presented in Table 1.

Table 1. The heat of combustion of the gelatin capsules.

$$e^\circ(\text{calor}) = 1360.40 \pm 0.20 \text{ cal/}^\circ\text{F}$$

$$e^f(\text{cont.}) = 2.16 \text{ cal/}^\circ\text{F}$$

$$\Delta E_\Sigma = 2.79 \text{ cal/g}$$

$$-\Delta nRT = 1.87 \text{ cal/g}$$

m (g)	Δt ($^\circ\text{F}$)	ΔE_{ign} (cal)	ΔE_{dec}^f (HNO_3)	ΔE_{dec}^f (H_2SO_4)	$-\Delta e_b$ (cal/g)
0.6073	2.040	11.34	8.65	4.77	4534.64
0.6233	2.099	17.92	9.48	4.90	4536.57
0.6228	2.098	20.02	9.99	4.89	4533.85
0.6214	2.085	10.96	8.28	4.88	4532.92
0.6091	2.045	9.80	9.88	4.79	4534.42
0.6111	2.052	13.02	9.55	4.80	4530.41

$$-\Delta e_c^\circ = -\Delta e_b - \Delta E_\Sigma = 4531.01 \pm 0.84^a \text{ cal/g}$$

$$-\Delta h_c^\circ = 4532.88 \text{ cal/g}$$

^a Standard deviation of the mean.

Calculations: To obtain the weights *in vacuo* (m) the weights of the samples (m) in air were multiplied by the following factors based on the densities of the compounds at 20°C:

4,4,6-trimethyl-1,3-dioxane	1.00116
<i>cis</i> -4,6-dimethyl-1,3-dioxane	1.00115
<i>trans</i> -4,6-dimethyl-1,3-dioxane	1.00111
2,2-dimethyl-1,3-dioxane	1.00111

The heats of combustion were calculated from equation

$$-\Delta E_c^\circ = 10^3 \frac{M}{m} [(e^\circ(\text{calor}) + e^f(\text{cont.}))\Delta t - \Delta E_{\text{ign}} - \Delta E_{\text{dec}}^f(\text{HNO}_3) - \Delta E_{\text{dec}}^f(\text{H}_2\text{SO}_4) + m' \Delta e_c^\circ(\text{gel}) - \Delta E_\Sigma] \quad (1)$$

where M is the molecular weight of the compound in question, m the mass of the sample *in vacuo*, $e^\circ(\text{calor})$ energy equivalent of the standard calorimeter system (cal/°F), $e^f(\text{cont.})$ contribution to the total energy equivalent from the contents of the bomb after combustion (cal/°F),^{5,9} ΔE_{ign} the correction due to the burnt ignition wire (cal), $\Delta E_{\text{dec}}^f(\text{HNO}_3)$ the correction due to the formation of nitric acid (cal), $\Delta E_{\text{dec}}^f(\text{H}_2\text{SO}_4)$ the correction due to the formation of sulfuric acid (cal), $m' \Delta e_c^\circ(\text{gel})$ the energy evolved by combustion of the gelatin capsule (cal), and ΔE_Σ so-called Washburn correction (cal).^{5,9}

Table 2. The combustion data of 4,6-dimethyl-1,3-dioxanes.

$$e^\circ(\text{calor}) = 1360.40 \pm 0.20 \text{ cal/}^\circ\text{F}$$

$$-\Delta e_c^\circ(\text{gel}) = 4531.01 \pm 0.84 \text{ cal/g}$$

$$t_h = t_i = 25.00^\circ\text{C}$$

m g	m' g	Δt °F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3 + \text{H}_2\text{SO}_4)$ cal		ΔE_Σ cal	$e^f(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal/g
<i>cis</i> -4,6-Dimethyl-1,3-dioxane				M = 116.16				
0.57215	— ^a	3.121	11.20	8.85	+	—	1.50	2.26
0.69960	— ^a	3.826	17.08	13.02	+	—	1.92	2.32
0.75136	— ^a	4.107	20.44	13.92	+	—	2.09	2.35
0.55284	0.1200	3.422	17.64	10.83	+	0.94	1.88	2.30
0.61380	0.1259	3.773	16.52	11.96	+	0.99	2.09	2.33
0.62362	0.1254	3.828	16.24	11.68	+	0.99	2.14	2.33
						$-\Delta E_c^\circ/M = 7399.56 \pm 2.04^b \text{ cal}\cdot\text{g}^{-1}$ $-\Delta E_c^\circ = 859.54 \pm 0.29^c \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_c^\circ = 860.72 \pm 0.57^d \text{ kcal}\cdot\text{mole}^{-1}$		
<i>trans</i> -4,6-Dimethyl-1,3-dioxane				M = 116.16				
0.51077	— ^a	2.801	10.22	12.26	+	—	1.29	2.22
0.60607	— ^a	3.318	8.54	10.58	+	—	1.63	2.28
0.82761	— ^a	4.539	14.84	22.68	+	—	2.31	2.38
0.59836	— ^a	3.284	13.44	15.35	+	—	1.57	2.27
0.58424	0.1267	3.627	18.34	11.49	+	0.99	1.95	2.31
0.28772	0.1202	1.985	15.54	7.44	+	0.95	0.93	2.16
						$-\Delta E_c^\circ/M = 7424.69 \pm 1.19^b \text{ cal}\cdot\text{g}^{-1}$ $-\Delta E_c^\circ = 862.46 \pm 0.21^c \text{ kcal}\cdot\text{mole}^{-1}$ $-\Delta H_c^\circ = 863.64 \pm 0.43^d \text{ kcal}\cdot\text{mole}^{-1}$		

^a Burnt in thin soda glass ampoules. ^b Standard deviation of the mean. ^c Over-all standard deviation. ^d Twice the over-all standard deviation.

The standard heats of combustion were calculated from equation

$$\Delta H_c^\circ = \Delta E_c^\circ + \Delta nRT \quad (2)$$

where Δn is the difference in the number of gaseous reactants and products.

The standard heats of formation, ΔH_f° (liq.) were calculated from standard heats of combustion assuming the values $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -94.052$ kcal/mole and $\Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) = -68.315$ kcal/mole recommended by the National Bureau of Standards.

In earlier reports^{1,2} the conditions were the same as above, but unfortunately the corrections to standard states have not been included. Consequently, we have recomputed the earlier results and the corrected values are presented in Tables 3–6. The results obtained in this work are presented in Tables 2 and 7.

Table 3. The corrected values of the heats of combustion presented in References 1 and 2.

$m_{\text{corr.}} = 0.99992m$ in Ref. 1 and 2 (due to erroneous density of air in Refs. 1 and 2).

<i>m</i> g	Δt °F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3)$ cal	ΔE_Σ cal	$e^f(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal/g
1,3-Dioxane						
				$M = 88.107$		
				$e^\circ(\text{calor}) = 1360.31 \pm 0.23$ cal/°F		
0.83286	3.888	14.28	18.25	2.36	2.37	6319.44
0.85108	3.968	6.16	12.18	2.41	2.39	6328.95
0.75528	3.521	5.60	20.10	2.08	2.33	6315.64
0.77660	3.623	12.60	10.72	2.16	2.35	6324.28
0.72935	3.404	9.80	14.34	1.99	2.32	6323.80
0.70472	3.293	16.38	17.18	1.90	2.30	6316.86
				$-\Delta E_c^\circ/M = 6321.50 \pm 2.07^b$ cal·g ⁻¹		
				$-\Delta E_c^\circ = 556.97 \pm 0.22^c$ kcal·mole ⁻¹		
				$-\Delta H_c^\circ = 557.56 \pm 0.43^d$ kcal·mole ⁻¹		
4-Methyl-1,3-dioxane						
				$M = 102.134$		
				$e^\circ(\text{calor}) = 1359.13 \pm 0.33$ cal/°F		
0.75753	3.899	15.68	14.31	2.11	2.34	6965.10
0.76854	3.955	14.20	16.85	2.14	2.34	6963.10
0.78065	4.020	11.62	20.29	2.17	2.34	6967.31
0.77184	3.976	14.00	19.30	2.15	2.34	6967.45
0.80268	4.124	7.84	13.46	2.23	2.36	6965.73
0.79898	4.127	19.18	20.27	2.22	2.35	6980.35
0.84793	4.364	17.92	23.66	2.36	2.37	6955.35
				$-\Delta E_c^\circ/M = 6966.34 \pm 2.82^a$ cal·g ⁻¹		
				$-\Delta E_c^\circ = 711.50 \pm 0.35^b$ kcal·mole ⁻¹		
				$-\Delta H_c^\circ = 712.39 \pm 0.69^c$ kcal·mole ⁻¹		
2-Methyl-1,3-dioxane						
				$M = 102.134$		
				$e^\circ(\text{calor}) = 1359.13 \pm 0.33$ cal/°F		
				$\Delta E_\Sigma = 2.78$ cal/g		
				$-\Delta E_c^\circ/M = 6918.62 \pm 2.42^a$ cal·g ⁻¹		
				$-\Delta E_c^\circ = 706.63 \pm 0.31^b$ kcal·mole ⁻¹		
				$-\Delta H_c^\circ = 707.52 \pm 0.62^c$ kcal·mole ⁻¹		

^a Standard deviation of the mean. ^b Over-all standard deviation. ^c Twice the over-all standard deviation.

Table 4. The corrected values of the heats of combustion presented in References 1 and 2.

 $m_{\text{corr.}} = 0.99992m$ in Refs. 1 and 2 (due to erroneous density of air in Refs. 1 and 2).

m g	Δt °F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^t(\text{HNO}_3)$ cal	ΔE_{Σ} cal	$e^t(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal·g ⁻¹
<i>cis</i> -2,4-Dimethyl-1,3-dioxane						
				M = 116.16		
				$e^\circ(\text{calor}) = 1359.13 \pm 0.33 \text{ cal/°F}$		
0.73554	4.023	9.52	10.97	2.11	2.35	7415.82
0.85248	4.667	6.58	21.35	2.53	2.39	7418.07
0.59999	3.295	18.06	13.97	1.61	2.27	7420.41
0.61380	3.372	14.00	18.45	1.66	2.27	7423.48
0.64725	3.551	7.28	21.59	1.78	2.28	7421.73
0.59147	3.251	17.50	9.46	1.58	2.27	7434.65
0.89662	4.894	11.20	14.08	2.70	2.43	7400.57
				$-\Delta E_c^\circ/M = 7419.25 \pm 3.85^a \text{ cal·g}^{-1}$		
				$-\Delta E_c^\circ = 861.83 \pm 0.50^b \text{ kcal·mole}^{-1}$		
				$-\Delta H_c^\circ = 863.01 \pm 1.01^c \text{ kcal·mole}^{-1}$		
4,5-Dimethyl-1,3-dioxane						
				M = 116.16		
				$e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/°F}$		
				$-\Delta E_{\Sigma} = 2.71 \text{ cal/g}$		
				$-\Delta E_c^\circ/M = 7447.19 \pm 0.95^a \text{ cal·g}^{-1}$		
				$-\Delta E_c^\circ = 865.08 \pm 0.24^b \text{ kcal·mole}^{-1}$		
				$-\Delta H_c^\circ = 866.26 \pm 0.48^c \text{ kcal·mole}^{-1}$		
5,5-Dimethyl-1,3-dioxane						
				M = 116.16		
				$e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/°F}$		
0.72841	3.998	10.50	18.76	2.07	2.33	7425.14
0.79990	4.398	20.16	15.48	2.33	2.37	7433.86
0.64222	3.529	11.90	18.87	1.76	2.29	7425.90
0.74003	4.061	12.88	14.21	2.11	2.34	7427.32
0.71510	3.933	18.88	19.25	2.02	2.32	7430.10
0.63121	3.466	18.76	9.79	1.73	2.29	7423.19
0.62530	3.435	8.96	19.78	1.70	2.28	7425.59
				$-\Delta E_c^\circ/M = 7427.30 \pm 1.33^a \text{ cal·g}^{-1}$		
				$-\Delta E_c^\circ = 862.76 \pm 0.27^b \text{ kcal·mole}^{-1}$		
				$-\Delta H_c^\circ = 863.94 \pm 0.53^b \text{ kcal·mole}^{-1}$		

^a Standard deviation of the mean. ^b Over-all standard deviation. ^c Twice the over-all standard deviation.

The purities of the compounds were checked with Shandon Universal gas chromatograph fitted with a 6-foot long copper tube containing Silocel C 22 as solid support and didecyl phthalate as stationary phase and a flame ionization detector. The carrier gas was composed of 75 % nitrogen and 25 % hydrogen and its flow rate was about 100 ml/min. The column temperature was in the range 64–120°C.

The final over-all precision of the ΔE_c° mean values was estimated following the scheme presented by Bjellerup¹¹ with two modifications. The quantity q_b was adopted from Månsson *et al.*¹² and our auxiliary material was gelatin and not an oil.

RESULTS AND DISCUSSION

The 1,3-dioxane ring exists mostly in the chair form (1),^{5,13,14} although some substituted derivatives may have stable flexible forms (2).^{13,14} It was recently estimated that the enthalpy difference between the chair and skew-

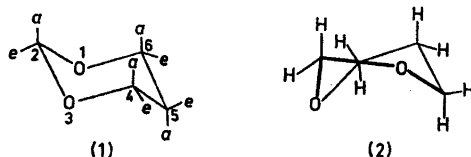
Table 5. The corrected values of the heats of combustion presented in References 1 and 2. $m_{\text{corr.}} = 0.99992m$ in Refs. 1 and 2 (due to erroneous density of air in Refs. 1 and 2).

<i>m</i> g	Δt F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3 + \text{H}_2\text{SO}_4)$ cal	<i>m'</i> g	$\Delta E\Sigma$ cal	$e^f(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal·g ⁻¹		
2, <i>cis</i>-4, <i>trans</i>-6-Trimethyl-1,3-dioxane				M = 130.188 $e^\circ(\text{calor}) = 1359.13 \pm 0.33 \text{ cal/°F}$ $\Delta E\Sigma = 2.63 \text{ cal·g}^{-1}$ $-\Delta E_c^\circ/M = 7822.42 \pm 1.54^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 1018.39 \pm 0.34^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 1019.87 \pm 0.68^c \text{ kcal·mole}^{-1}$					
2,2,4-Trimethyl-1,3-dioxane				M = 130.188 $e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/°F}$ $\Delta E\Sigma = 2.73 \text{ cal·g}^{-1}$ $-\Delta E_c^\circ/M = 7799.34 \pm 1.35^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 1015.38 \pm 0.30^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 1016.86 \pm 0.61^c \text{ kcal·mole}^{-1}$					
<i>cis</i>-2,2,4,6-Tetramethyl-1,3-dioxane				M = 144.2155					
0.66981	4.013	15.96	14.80	+	—	—	1.85	2.33	8103.31 ^d
0.65298	3.910	17.78	14.98	+	—	—	1.78	2.32	8094.52 ^d
0.53695	3.219	14.42	11.33	+	—	—	1.37	2.26	8106.13 ^d
0.57979	3.870	17.50	12.44	+	0.95	0.1202	1.73	2.33	8095.39 ^e
0.60703	3.634	10.22	16.52	+	—	—	1.60	2.29	8104.98 ^e
0.59471	3.973	20.02	12.66	+	0.97	0.1233	1.80	2.34	8099.87 ^e
0.47457	2.846	10.36	16.34	+	—	—	1.17	2.22	8100.44 ^d
				$e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/°F}$ $e^e(\text{calor}) = 1359.38 \pm 0.41 \text{ cal/°F}$ $-\Delta E_c^\circ/M = 8100.66 \pm 1.70^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 1168.24 \pm 0.41^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 1170.02 \pm 0.82^c \text{ kcal·mole}^{-1}$					

^a Standard deviation of the mean. ^b Over-all standard deviation. ^c Twice the over-all standard deviation. *m'* is the mass of gelatin capsule.

boat forms of the 1,3-dioxane ring is $6.8 \pm 0.7 \text{ kcal·mole}^{-1}$ using the heats of formation presented by Pihlaja and Heikkilä.^{13,1,2} Now it is possible to make more accurate evaluation from this energy difference with the aid of the corrected heats of formation in Tables 3–6.

Group increments: The heat of formation of gaseous cyclohexane is $-29.43 \text{ kcal·mole}^{-1}$ at 25°C. This value and the heat of formation of gaseous 1,3-dioxane,* $-83.42 \text{ kcal·mole}^{-1}$, can be used to estimate the increment to



* ΔH_{vap} is taken from Ref. 1.

Table 6. The corrected value of the heat of combustion of *trans*-2,2,4,6-tetramethyl-1,3-dioxane presented in Ref. 2.

$m_{\text{corr.}} = 0.99992m$ in Ref. 2 (due to erroneous density of air in Ref. 2).
 $^d e^\circ(\text{calor}) = 1360.31 \pm 0.23 \text{ cal/}^\circ\text{F}$
 $^e e^\circ(\text{calor}) = 1358.32 \pm 0.30 \text{ cal/}^\circ\text{F}$
 $^f e^\circ(\text{calor}) = 1359.38 \pm 0.41 \text{ cal/}^\circ\text{F}$
 $-\Delta e_c^\circ(\text{gel}) = 4522.37 \pm 2.86 \text{ cal/g}$
 $M = 144.2155$

m g	m' g	m'' g	Δt °F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3 + \text{H}_2\text{SO}_4)$ cal	ΔE_{Σ} cal	$e^f(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal·g ⁻¹		
0.54167 ^d	—	0.03153	3.441	14.70	16.58	+	1.48	2.27	8123.89	
0.46304 ^e	—	0.04027	3.021	16.38	6.16	+	1.39	2.25	8120.56	
0.53687 ^f	0.1213	0.04353	3.891	15.96	12.58	+	0.95	1.97	2.30	8131.72
0.53567 ^f	0.1235	0.04344	3.890	17.92	12.88	+	0.97	1.97	2.30	8125.93
0.55456 ^f	0.1288	0.04497	4.028	18.06	13.30	+	1.01	2.05	2.31	8121.26
0.51752 ^f	0.1237	0.04196	3.762	10.78	12.36	+	0.97	1.90	2.29	8110.59
$-\Delta E_c^\circ/M = 8122.32 \pm 3.11^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 1171.36 \pm 0.56^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 1173.14 \pm 1.13^c \text{ kcal·mole}^{-1}$										

^a Standard deviation of the mean. ^b Over-all standard deviation. ^c Twice the over-all standard deviation. m'' is the mass of *cis*-2,2,4,6-dimethyl-1,3-dioxane present as impurity.

Table 7. The combustion data of 2,2-dimethyl- and 4,4,6-trimethyl-1,3-dioxanes.

$e^\circ(\text{calor}) = 1360.40 \pm 0.20 \text{ cal/}^\circ\text{F}$
 $-\Delta e_c^\circ(\text{gel}) = 4531.01 \pm 0.84 \text{ cal·g}^{-1}$
 $t_h = t_i = 25.00^\circ\text{C}$

m g	m' g	Δt °F	ΔE_{ign} cal	$\Delta E_{\text{dec}}^f(\text{HNO}_3)$ cal	$\Delta E_{\text{dec}}^f(\text{H}_2\text{SO}_4)$ cal	ΔE_{Σ} cal	$e^f(\text{cont.})$ cal/°F	$-\Delta E_c^\circ/M$ cal·g ⁻¹
0.58434	0.1235	3.612	15.40	11.33	0.97	2.00	2.31	7414.94
0.66454	0.1255	4.047	8.68	11.23	0.99	2.29	2.36	7408.55
0.58785	0.1267	3.644	17.64	12.02	1.00	2.03	2.31	7415.10
0.62549	0.1316	3.859	14.00	12.71	1.04	2.17	2.33	7406.35
0.59846	0.1258	3.694	13.72	12.29	0.99	2.06	2.32	7410.43
0.60617	0.1281	3.748	17.22	11.97	1.01	2.09	2.32	7415.06
$-\Delta E_c^\circ/M = 7411.74 \pm 1.56^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 860.96 \pm 0.24^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 862.14 \pm 0.48^c \text{ kcal·mole}^{-1}$								
2,2-Dimethyl-1,3-dioxane								
M = 116.16								
0.48907	0.1225	3.230	17.22	10.40	0.96	1.68	2.27	7813.06
0.60961	0.1240	3.923	15.54	12.25	0.97	2.09	2.34	7797.36
0.61281	0.1260	3.952	18.06	12.44	0.99	2.11	2.34	7801.86
0.60840	0.1232	3.913	15.82	12.42	0.97	2.08	2.33	7795.65
0.60480	0.1305	3.917	16.24	12.30	1.03	2.09	2.34	7795.82
0.65837	0.1326	4.233	19.32	12.99	1.05	2.29	2.36	7795.21
$-\Delta E_c^\circ/M = 7799.83 \pm 2.83^a \text{ cal·g}^{-1}$ $-\Delta E_c^\circ = 1015.45 \pm 0.41^b \text{ kcal·mole}^{-1}$ $-\Delta H_c^\circ = 1016.93 \pm 0.83^c \text{ kcal·mole}^{-1}$								
4,4,6-Trimethyl-1,3-dioxane								
M = 130.188								

^a Standard deviation of the mean. ^b Over-all standard deviation. ^c Twice the over-all standard deviation.

Table 8. The standard heats of formation determined in this work or measured by other authors.

Compound	Ref.	$-\Delta H_f^\circ(\text{liq.})$, Obs.	kcal·mole ⁻¹ Calc.
1,3-Dioxane (I)	1	91.92 ± 0.43	—
4-Methyl (II)	1	99.44 ± 0.69	99.46
2-Methyl (VI)	1	104.32 ± 0.62	104.08
<i>cis</i> -2,4-Dimethyl (III)	1	111.19 ± 1.01	111.62
2,2-Dimethyl (V)	this work	112.06 ± 0.48	112.17
2,2,4-Trimethyl (X)	2	119.71 ± 0.61	119.71
5,5-Dimethyl (VIII)	1	110.26 ± 0.53	110.13
2, <i>cis</i> -4, <i>trans</i> -6-Trimethyl (IX)	1	116.70 ± 0.68	116.44
<i>cis</i> -2,2,4,6-Tetramethyl (XI)	2	128.92 ± 0.82	128.92 ^a
4,5-Dimethyl (XIV)	1	107.95 ± 0.48	108.02
<i>trans</i> -2,2,4,6-Tetramethyl (XIIB)	2	125.79 ± 1.13	—
<i>cis</i> -4,6-Dimethyl (IV)	this work	113.48 ± 0.57	113.48 ^a
<i>trans</i> -4,6-Dimethyl (VII)	this work	110.56 ± 0.43	110.76
4,4,6-Trimethyl (XIII)	this work	119.64 ± 0.83	119.0

^a As these are the only acetonal and formal with the biased diequatorial system, the differences vanish automatically.

ΔH_f° (g) resulting from the replacement of a $-(\text{CH}_2)_2$ -grouping in cyclohexane by an $-\text{CH}_2-\text{O}$ -grouping. This increment is -36.81 ± 0.35 kcal·mole⁻¹ in good agreement with the values reported by Månsson *et al.*¹² on the basis of the enthalpies of formation of gaseous trioxane and tetroxane. In connection with the recent investigation on aliphatic oxygen compounds¹⁵ it was observed that the derived bond-bond interaction scheme which suits well for aliphatic alcohols, ethers and acetals is less effective for some "oxanes". In a forthcoming paper a more detailed discussion of this discrepancy will be given.¹⁶

In the preceding papers^{1,2} some group increments to the heats of formation of gaseous 1,3-dioxanes at 25°C were presented. In this work group increments to the heats of formation of liquid 1,3-dioxanes were calculated in order to clarify their conformational energies in the liquid state.

The contributions of axial and equatorial methyl groups at the same position differ from each other since an axial methyl group at position 2, 4, or 6 interacts strongly with the axial hydrogen at the two other positions. An axial methyl group at position 5 leans outward, because the ring is flattened in the C₄₋₅₋₆ region and as a result its distance from the sterically interacting ring atoms increases.¹⁴ Moreover, the axial methyl group at position 5 interacts only with the electron pairs of the oxygen atoms and the value of this interaction has been found to be about 0.84 kcal·mole⁻¹.^{5,14,17}

From the studied compounds 1,3-dioxane (I), 2,2-dimethyl-1,3-dioxane (V), *trans*-4,6-dimethyl-1,3-dioxane (VII) and 5,5-dimethyl-1,3-dioxane (VIII) are equilibrium mixtures of two superposable and equally populated conformations, whereas *cis*-2,4-dimethyl-1,3-dioxane (III), *cis*-4,6-dimethyl-1,3-dioxane (IV), 4,4,6-trimethyl-1,3-dioxane (XIII), 2,*cis*-4,*trans*-6-trimethyl-1,3-dioxane

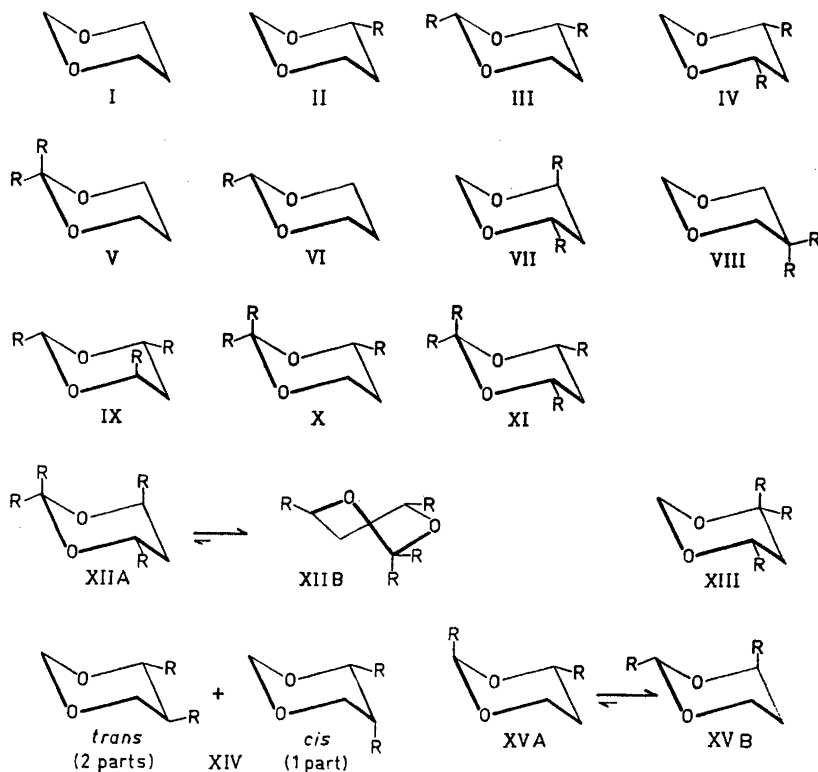


Fig. 1. The predominating conformations of the studied 1,3-dioxanes. (R is methyl).

(IX) and *cis*-2,2,4,6-tetramethyl-1,3-dioxane (XI) have only one biased conformation. 4-Methyl-1,3-dioxane (II), 2-methyl-1,3-dioxane (VI) and 2,2,4-trimethyl-1,3-dioxane (X) exist predominantly in the equatorial conformation^{5,14} and 4,5-dimethyl-1,3-dioxane is a mixture of *cis* (*ea*) and *trans* (*ee*) configurations (ab. 1:2, XIV).¹⁸ *trans*-2,2,4,6-Tetramethyl-1,3-dioxane (XII) has the skew-boat form.^{13,14}

In order to derive expressions for the compilation of the different group contributions the following abbreviations are used:

x_1 = the group increment to ΔH_f° (liq.) of an equatorial methyl group at positions 4 and 6,

x_2 = the group increment to ΔH_f° (liq.) of an equatorial methyl group at position 2.

x_3 = the interaction enthalpy of an axial methyl group and an axial hydrogen atom at positions 2 and 4 (or *vice versa*),

x_4 = the interaction enthalpy of an axial methyl group and an axial hydrogen atom at positions 4 and 6 (or *vice versa*) = approximately the interaction enthalpy between two equatorial or equatorial and axial methyl groups at positions 4 and 5 (or *vice versa*).

x_5 = the group increment to ΔH_f° (liq.) of an equatorial methyl group at position 5, and

x_6 = the stabilizing effect of the biased diequatorial system in *cis*-2,2,4,6-tetramethyl-1,3-dioxane.

H_I, H_{II} etc. are equal to the heats of formation of the corresponding 1,3-dioxanes.

From the heat of formation of 5,5-dimethyl-1,3-dioxane the value of x_5 is obtained directly, since

$$2x_5 = H_{VIII} - H_I - 0.84 = -110.26 + 91.08 \pm 0.96 = -19.18 \pm 0.96$$

and x_5 is -9.59 ± 0.48 kcal·mole⁻¹. The value, 0.84 kcal·mole⁻¹, in the above equation corresponds the interaction enthalpy of the axial methyl group at position 5.^{5,14,17}

Similarly we obtain

$$\begin{aligned} x_1 &= H_{II} - H_I; & x_2 &= H_{VI} - H_I; & x_1 + x_2 &= H_{III} - H_I; \\ 2x_1 + x_2 + x_3 + x_4 &= H_{IX} - H_I; & x_1 + 2x_2 + 2x_3 &= H_X - H_I; \\ 2x_1 + 2x_2 + 2x_3 + x_6 &= H_{XI} - H_I; & 2x_2 + 2x_3 &= H_V - H_I \end{aligned}$$

On the basis of the heats of formation of *cis*- and *trans*-4,6-dimethyl-1,3-dioxanes the following expression is obtained

$$x_3 + x_4 = H_{VII} - H_{IV}$$

The heat of formation of the 1:2 mixture of *cis*- and *trans*-4,5-dimethyl-1,3-dioxanes leads to equation

$$x_1 + x_4 + x_5 = H_{XVI} - H_I - 0.33 \times 0.84$$

and after rearrangement and partial solution of the above expressions the following set of equations is derived

$$\begin{aligned} x_1 & & & = -7.52 \\ & x_2 & & = -12.40 \\ x_1 + x_2 & & & = -19.27 \\ 2x_1 + x_2 + x_3 + x_4 & & & = -24.78 \\ x_1 + 2x_2 + x_3 + x_4 & & & = -27.79 \\ & & x_3 + x_4 & = 2.92 \\ 2x_1 + 2x_2 + 2x_3 + x_6 & & & = -37.00 \\ & & x_5 & = -9.59 \\ & x_2 + x_3 & & = -10.07 \\ x_1 & & + x_4 + x_5 & = -16.31 \end{aligned} \quad (3)$$

The optimum group increments were then determined on an IBM 1130 computer using a linear regression program with a least squares fit.¹⁵ Table 8 lists the heats of formation of 1,3-dioxanes and Table 9 the compiled group increments and their standard errors.

From these group increments and the heat of formation of *cis*-4,6-dimethyl-1,3-dioxane we can calculate the group contribution of an equatorial methyl group in this biased diequatorial system to be

$$\begin{aligned} H_{IV} - H_I - 2x_1 &= (-113.48 + 91.92 + 15.08)/2 \pm 0.70 \\ &= -3.24 \pm 0.70 \text{ kcal·mole}^{-1} \end{aligned}$$

Table 9. The compiled group increments to $\Delta H_f^\circ(\text{liq.})$ of methyl-substituted 1,3-dioxanes.

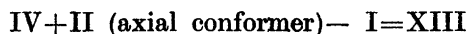
Group		Increment, kcal-mole ⁻¹	
CH ₃ :	4e (without 6-Me)	x_1	- 7.54 ± 0.19
	2e	x_2	- 12.16 ± 0.24
	$\Delta(2e - 2a)/2$	x_3	+ 2.035 ± 0.23
	2a	$x_3 - 2x_3$	- 8.09 ± 0.24
	4a (without 6-Me)	$x_1 - x_3 - x_4$	- 4.82 ± 0.24
	$\Delta(4e - 4a) - x_3$	x_4	+ 0.69 ± 0.29
	5e	x_5	- 9.52 ± 0.24
	4e (with 6e) in acetoneals	$x_1 + (x_6/2)$	- 8.37 ± 0.42
RMS ^a 0.30 kcal-mole ⁻¹			
	4e (with 6-Me) in formals	$(H_{IV} - H_I)/2$	- 10.78 ± 0.50
	4e (with 6-Me) in acetals		- 7.54 ± 0.19
	5a	$x_5 + 0.84$	- 8.68 ± 0.30
	4a (with 6e) in formals	$H_{VII} - H_I + 10.78$	- 7.86 ± 0.46
	4a (with 6e) in acetals		- 4.82 ± 0.24
(CH ₃) ₂ :	4e, 4a		- 0.7 ^b
	4e, 5e or 4a, 5e or 4e, 5a	x_4	+ 0.69 ± 0.29

^a Root Mean Square deviation of each correlation. ^b Calculated by the bond-bond interaction scheme of Pihlaja and Kankare.¹⁵

greater than the usual value -7.54 ± 0.19 kcal-mole⁻¹. This may be due to the fact that the puckering of the 1,3-dioxane ring (as chair form) decreases in the order 4,6-diequatorially substituted formal > 4,6-diequatorially substituted acetal > 4,6-diequatorially substituted acetal, since a single methyl substituent at position 2 flattens the ring appreciably. This conclusion is in good agreement with the results described in Table 9 which show that the group contribution of an equatorial methyl group at position 4 in 2, *cis*-4, *trans*-6-trimethyl-1,3-dioxane does not differ significantly from the value -7.54 ± 0.19 kcal-mole⁻¹, whereas the value of this increment in *cis*-2,2,4,6-tetramethyl-1,3-dioxane is

$$x_1 + x_6/2 = 7.54 + 0.83 \pm 0.42 = 8.37 \pm 0.42 \text{ kcal-mole}^{-1}.$$

By using the bond-bond interaction scheme described recently by Pihlaja and Kankare¹⁵ it is possible to evaluate the enthalpy change for the following reaction



in the gaseous state and the value $\Delta H = -0.7$ kcal-mole⁻¹ is obtained.

When assuming that the enthalpy difference for the above reaction in the liquid state is approximately equal to that in the gaseous state the heat of formation of 4,4,6-trimethyl-1,3-dioxane can be estimated, since

$$\begin{aligned} H_{\text{XIII}} &= H_{\text{IV}} + x_1 + x_3 + x_4 - 0.7 \\ &= -113.48 - 7.54 + 2.04 + 0.69 - 0.7 \\ &= -119.0 \text{ kcal-mole}^{-1} \end{aligned}$$

in agreement with the experimentally obtained value -119.64 ± 0.83 kcal-mole⁻¹.

Conformational energies. Eliel and Knoeber¹⁴ recently obtained the value 138 ± 6 for the constant of the equilibrium between the *cis* and *trans* forms of 2,4-dimethyl-1,3-dioxane and hence $-\Delta G^\circ = 2.92 \pm 0.02$ kcal-mole⁻¹ for these isomers. *cis*-2,4-Dimethyl-1,3-dioxane exists in the biased diequatorial chair conformation, but *trans*-2,4-dimethyl-1,3-dioxane may exist in two conformations (XVA and XVB, Fig. 1) in which either the methyl group in position 2 or the methyl group in position 4 is axially orientated. The conformational energy of an axial methyl group in position 2 is equal to $2x_3 = 4.07$ kcal-mole⁻¹ (Tables 9 and 10) and that of an axial methyl group in position 4 equal to 2.92 ± 0.50 kcal-mole⁻¹ (experimentally obtained value) or 2.72 ± 0.52 kcal-mole⁻¹ (compiled value, Tables 9 and 10). Consequently, the difference in the stabilities of the conformers of *trans*-2,4-dimethyl-1,3-dioxane is about 1.15–1.35 kcal-mole⁻¹ and thus the proportion of the *a,e* conformer is about 10 %. This result is in good agreement with the assumption of Eliel and Knoeber¹⁴ that the ratio XVB/XVA is in excess of 5:1 and quite possibly as high as 10:1.

Table 10. The conformational energies or interaction enthalpies of methyl groups at different positions in the 1,3-dioxane ring.

Orientation of the methyl groups	Conformational energy or interaction enthalpy, kcal-mole ⁻¹	Ref.
2a	$2x_3 = 4.07 \pm 0.46$ ~ 3.55	This work 14
4a	$x_3 + x_4 = 2.72 \pm 0.52$	This work
4a	$H_{VII} - H_{IV} = 2.92 \pm 0.50$	This work
4a	2.92 ± 0.02^a	14
	2.77 ± 0.08^a	14
	2.73 ± 0.02^a	14
	2.87 ± 0.04^a	14
5a	0.80	5,14
	0.97	14
	0.89	17
4e,5e or 4a,5e or 4e,5a	0.69 ± 0.29	This work
2a,4a	ab. 8.9^b	5
4a,6a	ab. $3.0 - 4.0^b$	This work
ΔH° (skew-boat — chair)	$7.2_0 \pm 0.9_4$ $7.2_0 \pm 0.7_6$ $6.8_0 \pm 0.5_8$ Mean 7.1 ± 0.8	This work 13
ΔS° (skew-boat — chair)	4.8 ± 1.0^c 3.9 ± 0.5^c	This work 5,13
ΔG° (skew-boat — chair)	5.7 ± 0.6 5.6 ± 0.6	This work 13

^a By equilibration of the *cis* and *trans* isomers of 2,4-dimethyl-, 2-ethyl-4-methyl-, 2-vinyl-4-methyl- and 2-*t*-butyl-4-methyl-1,3-dioxanes, respectively. ^b Estimations. ^c cal.deg.⁻¹mole⁻¹.

From the above data we can calculate the value $-2.84 \text{ kcal}\cdot\text{mole}^{-1}$ for ΔG° between *cis*- and *trans*-2,4-dimethyl-1,3-dioxanes which differs only slightly from the experimentally obtained result.¹⁴

The energy difference between the chair and skew-boat forms of the 1,3-dioxane ring. Using the scheme described earlier¹³ it is found that (a) assuming that 2,2-dimethyl-1,3-dioxane exists predominantly in the chair form ($\geq 95\%$)

$$-\Delta G^\circ_{c\leftrightarrow s} = 4.07 + RT \ln 19 = 5.82 \pm 0.46 \text{ kcal}\cdot\text{mole}^{-1}$$

(b) the heats of formation of isomeric 2,2,4,6-tetramethyl-1,3-dioxanes differ by $3.13 \pm 0.97 \text{ kcal}\cdot\text{mole}^{-1}$. *cis*-2,2,4,6-Tetramethyl-1,3-dioxane exists predominantly in the chair form^{13,14} (Fig. 1), whereas there is a strong interaction between the axial methyl groups at positions 2 and 6 in the chair form (XIIA) of *trans*-2,2,4,6-tetramethyl-1,3-dioxane. It was concluded earlier^{5,13,14} that the *trans* isomer has the skew-boat form (XIIB) in which, of the diaxial interactions in the chair form, only about $0.6 \text{ kcal}\cdot\text{mole}^{-1}$ remains.¹³ However, we think now that the interactions in *trans*-2,2,4,6-tetramethyl-1,3-dioxane are mainly due to the skew-boat form.¹⁰ Consequently

$$\Delta H_{c\leftrightarrow s} = 3.13 + 4.07 \pm 0.94 = 7.20 \pm 0.94 \text{ kcal}\cdot\text{mole}^{-1}$$

(c) On the basis of the barrier to internal rotation ($2.72 \pm 0.14 \text{ kcal}\cdot\text{mole}^{-1}$) in dimethyl ether,¹⁹ the barrier to internal rotation in 1,3-dioxane is about $5.44 \pm 0.28 \text{ kcal}\cdot\text{mole}^{-1}$.

If it is assumed that the third estimate (c) represents most likely a free energy difference, the excess entropy of the skew-boat form is (a) $4.6 \pm 1.0 \text{ cal}\cdot\text{degr}^{-1}\cdot\text{mole}^{-1}$ and (c) $5.9 \pm 1.5 \text{ cal}\cdot\text{degr}^{-1}\cdot\text{mole}^{-1}$. An earlier estimation reports the value $3.9 \pm 0.5 \text{ cal}\cdot\text{degr}^{-1}\cdot\text{mole}^{-1}$. Obviously the excess entropy^{5,13} of the skew-boat form of 1,3-dioxane ring is close to that of the corresponding form of cyclohexane (ab. 5 E.U.) and thus the mean of the above values, $4.8 \pm 1.0 \text{ E.U.}$, seems to be valid to represent $-\Delta S^\circ_{c\leftrightarrow s}$ for the 1,3-dioxane ring.

The heats of formation measured in this work or adopted by other investigators are collected in Table 8 and the compiled group increments in Table 9. The estimated conformational energies are presented in Table 10.

With the aid of the presented group increments it is possible to calculate the heats of formation of liquid methyl-substituted 1,3-dioxanes fairly accurately (Table 8). The values of the interaction energies of the axial methyl groups obtained in this work are generally in good agreement with those reported by Eliel and Knoeber¹⁴ and the small deviations may be due to experimental errors.

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