Bond-bond Interactions in Organic Oxygen Compounds

Part IV. An Extension of the Bond-bond Interaction Scheme for Aliphatic Alcohols and Ethers to Acetals and Orthoesters. Correlation between the Enthalpies of Formation and Numbers of Carbon Atoms for Normal Alkanols. Ring Strain in Cyclic Ethers and Acetals

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A bond-bond interaction scheme, previously presented for aliphatic alcohols and ethers,[1] has been extended to aliphatic acetals and orthoesters. This extension is based on recent determinations of the enthalpies of formation of several acetals and some orthoesters. The linear dependence of the enthalpies of formation of gaseous normal alkanols on carbon numbers gave for the heat of formation of gaseous hexadecanol the value -126.5 kcal/mol, which is in good agreement with the value -126.8 kcal/mol derived using the extended bond-bond interaction scheme.

The evaluated ring strains for several "oxanes" are in general agreement with previous results, but show several irregularities. For instance, the apparent ring strains in 1,3-dioxanes are almost negligible, although these compounds include a rabbit-ear effect. Generally, the ring strains in "oxanes" deviate only slightly from those in cyclanes, showing that the increased angular strain in the former series of compounds is offset by the decreased non-bonded interactions.

In the first part of this series of papers, Kankare and this author[1] derived an Allen-type bond-bond interaction scheme for gaseous aliphatic alcohols and ethers, and carried out some preliminary computations for acetals. Later, the number of accurate values of the enthalpies of formation of acetals have greatly increased, and also the enthalpies of formation of gaseous methyl and ethyl orthoformates have become available, making possible the extension of the scheme to these series of compounds.[2-11]

The correlation between the enthalpies of formation of gaseous normal alkanols and carbon numbers may serve as an independent method of testing the significantly different values reported for the enthalpies of formation of some of these compounds. The evaluation of apparent ring strains for "oxanes" may also give valuable information about the effect of oxygen as a heteroatom in cyclic compounds.

1. G e n e r a l   t r e a t m e n t

The aim of the computation was to adjust the coefficients in the equation

$$\Delta H_a{}^0(g) - \sum E_b(g) = n_1 \Gamma_{CCC} + n_2 \Gamma_{CCO} + n_3 \Gamma_{COC} + n_4 \Gamma_{OCO} + n_5 \Delta_{CCC} +$$

$$n_6 \Delta_{CCO} + n_7 \Delta_{OCO} + n_8 \Delta_{OOO} + n_9 S_{15}{}^{HH} + n_{10} S_{15}{}^{HO:} + n_{11} S_{16}{}^{HH} \qquad (1)$$

where $\Delta H_a{}^0(g)$ is the heat of atomization of the compound in question, $\sum E_b(g)$ the sum of bond energies, the general term Γ_{ABC} the contribution of the interaction ABC, the general term Δ_{ABC} the contribution of the non-bonded trios attached to the same carbon atom, $S_{15}{}^{HH}$ the contribution of the non-bonded interaction between fifth-neighbor hydrogen atoms, $S_{15}{}^{HO:}$ the contribution of the non-bonded interaction between fifth-neighbor hydrogen atom and the lone pair orbital of an oxygen atom, and $S_{16}{}^{HH}$ the contribution of the non-bonded interaction between sixth-neighbor hydrogen atoms.[1] The values used for the heats of atomization of the elements and for the bond energies were those reported previously.[1]

The machine computation must be restricted to acyclic alcohols, ethers, and acetals, since the only available heats of formation of orthoesters are those of methyl and ethyl orthoformates.[6] Moreover, the orthoesters include at least two rabbit-ear effects.[6,12] A discussion of the group increment of an oxygen trio attached to the same carbon atom will be published separately.[6]

Table 1 lists the 35 compounds for which accurate standard heats of formation in the gaseous state were available at the time of computation. Also the numbers of $S_{15}{}^{HH}$, $S_{15}{}^{HO:}$ and $S_{16}{}^{HH}$ interactions are shown in Table 1.

The optimum values for the different group increments were determined on an IBM 1130 Computer at the Computer Center, University of Turku, Turku, using a linear regression program with a least-squares criterion.[1] Table 2 shows the group increments and their standard errors and the root-mean-square deviation of each correlation (RMS). The differences between the computed and the experimental results are presented in Table 1.

The agreement between the group increments derived in this work for aliphatic oxygen compounds and those presented earlier for alkanes by Kalb et al.[13] lead to the conclusion that it may be possible to derive a common scheme for alkanes and their oxygen-containing analogs. Also the agreement between the results reported in this paper and the preliminary results of Pihlaja and Kankare [1] is very satisfactory. Most of the approximate group increments reported by other authors are also consistent with the present calculations (Table 2), except the value -3.65 kcal/mol of Pilcher and Fletcher [8] for the group increment of an O,C,O-trio, attached to the same carbon atom. This discrepancy will be discussed later.

Heats of formation of methyl and ethyl orthoformates,[6] dimethoxymethane and 1,1-dimethoxyethane,[8] which became available after the machine computation, are presented together with some less accurate enthalpies of formation for acetals in Table 3. Using the general treatment (eqn. 1 and Table 2), the enthalpies of formation of methyl and ethyl orthoformates [6] gave the values -7.34 and -7.49 kcal/mol, respectively, for the total destabilization effect of an oxygen trio, attached to the same carbon atom.[6]

Table 1. Comparison of calculated and experimental data.

Compound	$-\Delta H_f^0(g)$ kcal/mol	$\Delta H_a^0(g) - \sum E_b(g)$ obs.	$\Delta H_a^0(g) - \sum E_b(g)$ calc.	Diff.^{a}	S_{15}^{HH}	S_{15}^{HO}:	S_{16}^{HH}	Ref.
EtOH	56.19	5.89	5.53	−0.36	0	0	0	1
PrOH	61.27	8.64	8.27	−0.37	0	0	0	14−16
i-PrOH	65.09	12.46	12.33	−0.13	0	1^b	0	1
BuOH	65.88	10.92	11.01	+0.09	0	0	0	15, 17, 18
i-BuOH	67.72	12.76	12.98	+0.22	0	1	0	1
s-BuOH	70.06	15.10	15.07	−0.03	0	1	0	1
t-BuOH	74.84	19.88	19.92	+0.04	0	2^b	0	1
1-Pentanol	70.66	13.37	13.74	+0.37	1	0	0	17
3-Me-1-BuOH	72.60	15.31	15.10	−0.21	1	1	0	1
2-Me-2-BuOH	79.11	21.82	22.04	+0.22	0	1^b	0	1
2-Pentanol	75.17	17.88	17.80	−0.08	1	1	0	1
2-Me-1-BuOH	72.20	14.91	14.95	+0.04	1	1	0	1
1-Hexanol	76.27	16.67	16.48	−0.19	0	0	0	14, 19
1-Heptanol	81.36	19.42	19.22	−0.20	0	0	0	19
1-Octanol	86.13	21.85	21.96	+0.11	0	0	0	19
1-Nonanol	91.61	25.00	24.70	−0.30	0	0	0	14
1-Decanol	96.15	27.21	27.44	+0.23	0	0	0	14, 19
MeOMe	43.99	5.86	5.90	+0.04	0	0	0	1, 24
MeOEt	51.73	11.27	11.43	+0.16	0	0	0	1
EtOEt	59.93	17.14	16.96	−0.18	0	0	0	1
PrOMe	56.82	14.03	14.17	+0.14	0	0	0	1
i-PrOMe	60.24	17.45	17.61	+0.16	0	0	0	1
t-BuOMe	70.0	24.88	24.58	−0.30	1	0	0	1
Pr₂O	69.99	22.54	22.43	−0.11	2	0	0	1
(i-Pr)₂O	76.4	28.95	29.31	+0.36	0	0	0	1
i-PrOBu-t	85.6	35.82	35.82	(±0.00)^c	2	0	1	1
Bu₂O	79.84	27.73	27.91	+0.18	1	0	0	1
(s-Bu)₂O	86.18	34.07	33.88	−0.19	3	0	0	1
CH₂(OEt)₂	99.11	36.09	35.93	−0.16	0	1	0	7
MeCH(OEt)₂	108.41	43.04	43.29	+0.25	1	2	0	2
MeCH(OPr-i)₂	125.70	55.67	55.79	+0.12	3	2	0	3
Me₂C(OMe)₂	102.9	39.86	39.68	−0.18	2	1	0	25
Et(OCH₂)₃Me	138.89	55.60	54.90	−0.70	2	2	0	7
Et(OCH₂)₄Me	177.10	73.56	73.87	+0.31	0	4	0	7
Et(OCH₂)₅Me	216.52	92.73	92.84	+0.11	0	6	0	7
						8		

^{a} ΔH_f^0 (g, exptl.) $- \Delta H_f^0$ (g, calc.). ^{b} Erroneously assigned to 0 in Ref. 1. ^{c} Because this is the only compound with an S_{16}^{HH} interaction, the difference vanishes automatically.

Table 2. Optimum values of group increments, determined in this work and in those presented by Kalb *et al.*,[13] Skinner,[18] Pilcher and Fletcher,[8] and Pihlaja and Kankare.[1]

Increment	The enthalpy increments for different groups in kcal·mol⁻¹				
	This work	Kalb *et al.*[a]	Skinner	Pilcher and Fletcher	Pihlaja and Kankare
Γ_C	2.33	2.323±0.118	2.35	—	2.33
Γ_{CCC}	2.738±0.023	2.673±0.117	2.58	—	2.737±0.038
Γ_{CCO}	5.530±0.024	—	5.66	—	5.623±0.127
Γ_{COC}	5.897±0.133	—	6.00	5.90	5.725±0.199
Γ_{OCO}	13.365±0.321[b]	—	—	12.96	13.4 ±0.5
Δ_{CCC}	−0.620±0.163	−0.819±0.099	−0.55	—	−0.640±0.210
Δ_{CCO}	−1.324±0.090	—	−1.43	—	−1.465±0.139
Δ_{OCO}	−2.936±0.160	—	—	−3.65	−2.8 ±0.5
$S_{15,HH}$	−0.765±0.100	−0.687±0.056	—	—	−0.669±0.126
$S_{15,HO:}$	−0.146±0.129	—	—	—	−0.252±0.200
$S_{16,HH}$	−1.997±0.409	−2.552±0.609	—	—	−1.802±0.466
RMS	±0.2796	±0.0185[c]	—	—	±0.0135[c]

[a] Six parameters. [b] Månsson[7] reported the value 12.93 kcal/mol. [c] In kcal·mol⁻¹ bond⁻¹.

Table 3. Experimental and calculated values of enthalpies of formation of some ortho-
esters and acetals not included in the computation of the group increments.

Compound	$-\Delta H_f^0(g)$, kcal mol^{-1}		Diff.[a]	Ref.
	Obs.	Calc.		
$CH_2(OCH_3)_2$	83.21	83.25	$+0.04$	8
$CH_3CH(OCH_3)_2$	93.15	92.94	-0.21	8
$CH(OCH_3)_3$	128.41	128.33	-0.08	6
$CH(OCH_2CH_3)_3$	151.84	151.91	$+0.07$	6
$(CH_3)_3C(OCH_2CH_3)_2$	120.5	118.44	-2.06	25
$CH_2(OCH_2CH_2CH_2CH_3)_2$	117.5	119.24	$+1.74^b$	3,11
$EtCH(OCH_2CH_2CH_2CH_3)_2$	132.10	133.85	$+1.75^b$	3

[a] ΔH_f^0(g, exptl.) $-\Delta H_f^0$(g, calc.). ^{b} The nearly equal deviations between the experimental
and calculated values of these compounds may also be due to an excess destabilization effect,
which exists in acetals when the alkoxy chains are long enough.[3] If we assume that these com-
pounds attain the *anti* form (Fig. 1), they include two rabbit-ear effects but no S_{18}^{HO} interac-
tions. This assumption gives the calculated values 117.53 and 132.14 kcal/mol, respectively,
using the value -1.0 kcal/mol per rabbit-ear effect.[6] The excellent agreement with the experi-
mental results in the latter case makes it reasonable to propose *anti* conformation for 5,7-dioxa-
undecane and 6-ethyl-5,7-dioxaundecane.

The preliminary results for acetals [1] are in general agreement with those
obtained in this work (Table 2). The number of different S-interactions differs
slightly from that in the previous work [1] because of corrections due to the fact
that dimethoxymethane and its homologs (Fig. 1) exist predominantly in the
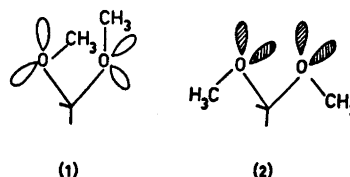*gauche* form to avoid the rabbit-ear effects.[12]

Fig. 1. The predominant *gauche* (1) and
the unfavored *anti* (2) conformations of
dimethoxymethane or its homologs.

The enthalpies of formation of dimethoxymethane (1) and 1,1-dimethoxy-
ethane (2), reported recently by Pilcher and Fletcher,[8] were not included in
the machine computation and may hence serve to test the derived group
increments (see p. 458).
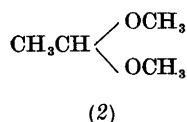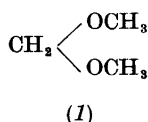
2. Enthalpies of formation of alkanols

The values collected in Ref. 1, except those for 1-propanol, 1-butanol,
1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, and 1-decanol, were adopted.

The mean of the values reported by Chao and Rossini,[14] Snelson and Skinner,[15] and Lewis and Head [16] was regarded as the best value for the enthalpy of formation of 1-propanol. Similarly, the mean of the values of Gundry et al.[17] and Snelson and Skinner [15,18] was accepted for 1-butanol. The enthalpy of formation of 1-pentanol was taken from the recent paper of Gundry et al.[17] The values for 1-hexanol and 1-decanol are the means of the results reported by Chao and Rossini,[14] and Verkade and Coops,[19] the values of the latter authors being corrected according to recent recommendations.[20] The enthalpies of formation of 1-heptanol and 1-octanol, reported by Verkade and Coops,[19] seem to be reliable after revision in terms of the presently accepted atomic weights and the corrected value for the heat of combustion of benzoic acid standard.[17,20] The adopted enthalpy of formation of 1-nonanol was that reported by Chao and Rossini.[14]

To derive the enthalpies of formation of the above normal alkanols in the gaseous state, the heats of vaporization for 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, obtained by Wadsö,[21] were taken. The line, plotting his series of enthalpies of vaporization for normal alkanols, was extrapolated using the mean increment of 1.13 kcal/mol per methylene group to obtain estimates of ΔH_{vap} for 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol. The data for normal alkanols are collected in Table 4.

Table 4. Enthalpies of formation and vaporization of normal alkanols.

Alkanol	$-\Delta H_f^0(l)$ kcal/mol	ΔH_{vap} [21] kcal/mol	$-\Delta H_f^0(g)$ kcal/mol	Calculated values		Ref.
				Eqn. (2)	Eqn. (3)	
Ethanol	—	—	56.19	55.82	56.03	1
Propanol	72.58	11.31	61.27	60.89	61.06	14 – 16
Butanol	78.38	12.50	65.88	65.96	66.10	15, 17, 18
Pentanol	84.27	13.61	70.66	71.02	71.13	17
Hexanol	91.00	14.73	76.27	76.09	76.17	14, 19
Heptanol	97.22	15.86	81.36	81.16	81.20	19
Octanol	103.12	16.99	86.13	86.23	86.24	19
Nonanol	109.73	18.12	91.61	91.30	91.27	14
Decanol	115.40	19.25	96.15	96.36	96.30	14, 19

The following equation may be derived on the basis of the computed group increments for the direct calculation of the enthalpies of formation of gaseous alkanols:

$$-\Delta H_f^0(g, \text{alkanol}) = 45.63 + 2.33 n_C + 2.74 n_1 + 5.53 n_2 - 0.62 n_5 - 1.32 n_6 -$$
$$0.765 n_9 - 0.15 n_{10} - 2.00 n_{11} \tag{2}$$

where n_C is the number of carbon atoms and 2.33 kcal/mol the value of the increment for each additional carbon atom.

A good linear correlation prevails between the enthalpies of formation of the gaseous normal alkanols and the number of carbon atoms when $n_C \geq 2$ (Fig. 2).[17] The expression

$$-\Delta H_f^0(g, \ n\text{-alkanol}) = (5.034 \pm 0.035)n_C + (45.963 \pm 0.231) \tag{3}$$

was derived for the straight line in Fig. 2 by the method of least squares (Table 4).

To compare eqns. (2) and (3), the enthalpy of formation of gaseous 1-hexadecanol was calculated. The values 126.8 and 126.5 kcal/mol, respectively, were obtained. Gundry et al.[17] reported the value 123.7 kcal/mol, which deviates greatly from both estimates. Also the value 85.3 kcal/mol, determined by the
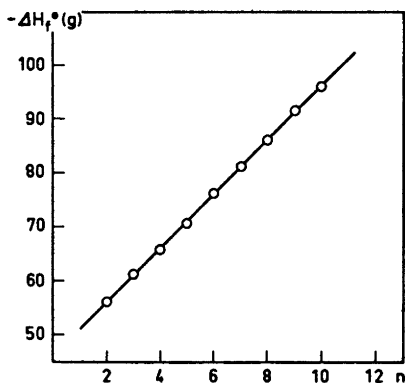

Fig. 2. The dependence of the enthalpies of formation of gaseous normal alkanols on the number of carbon atoms.
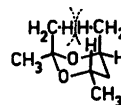

Fig. 3. The crowding between the axial methyl groups of *trans*-2,2,4,6-tetramethyl-1,3-dioxane in its unstable chair form.

latter authors for the enthalpy of formation of gaseous 1-octanol, differs about 1 kcal/mol from the calculated value 86.2 kcal/mol (eqns. 2 and 3), whereas the corrected value 86.1 kcal/mol of Verkade and Coops [19] agrees closely with the computed one.

3. Enthalpies of formation of ethers

For ethers, the values given in Ref. 1 were accepted (Table 1). The computed coefficients yield the following equation for the direct calculation of the enthalpies of formation of gaseous ethers:

$$-\Delta H_f^0(g, \ \text{ether}) = 33.47 + 2.33n_C + 2.74n_1 + 5.53n_2 + 5.90n_3 - 0.62n_5 -$$
$$1.32n_6 - 0.765n_9 - 0.15n_{10} - 2.00n_{11} \tag{4}$$

The only available enthalpy of formation for acyclic ethers which has not been used in the computation of the above group increments (Table 2) is that for di-*t*-butyl ether, -87.2 kcal/mol.[22] Two severe interactions between sixth-neighbor hydrogen atoms which, moreover, are locked, exist in this molecule. The situation may be compared with that in the chair form of *trans*-2,2,4,6-tetramethyl-1,3-dioxane (Fig. 3), of which the magnitude of the 1,3-diaxial interaction in the liquid state has been estimated to be about 8.9

kcal/mol.[10],[23] The difference between the calculated (eqn. 4) and experimental enthalpies of formation of gaseous di-*t*-butyl ether is about 11 kcal/mol or about 5.5 kcal/mol per interaction. This value is in reasonable agreement with the above value for cyclic systems, when it is taken into account that several interactions have been shown to be less pronounced in acyclic systems.[6],[12]

4. Enthalpies of formation of acetals

The only available accurate data for acetals at the time of computational work were those of Månsson [7] for diethoxymethane, 3,5,7-trioxanonane, 3,5,7,9-tetraoxaundecane and 3,5,7,9,11-pentaoxatridecane, that of Stern and Dorer [25] for 2,2-dimethoxypropane, that of Pihlaja and Heikkilä [2] for 1,1-diethoxyethane, and that of Pihlaja and Launosalo [3] for 2,4,6-trimethyl-3,5-dioxaheptane (Table 1). Less accurate values are available for 2,2-diethoxy-propane,[25] 5,7-dioxaundecane,[11] and 6-ethyl-5,7-dioxaundecane [3] (Table 3). Quite recently, Pilcher and Fletcher [8] determined the enthalpies of formation of gaseous dimethoxymethane and 1,1-dimethoxyethane (Table 3). These values fit into the derived scheme extremely well (see below).

The computed group increments lead to the following equation for the direct calculation of the enthalpies of formation of gaseous acetals:

$$- \Delta H_f^0(\text{g, acetal}) = 51.39 + 2.33 n_C + 2.74 n_1 + 5.53 n_2 + 5.90 n_3 +$$
$$13.365 n_4 - 0.62 n_5 - 1.32 n_6 - 2.94 n_7 - 0.765 n_9 - 0.15 n_{10} - 2.00 n_{11} \qquad (5)$$

To test the above equation, the enthalpies of formation of dimethoxymethane and 1,1-dimethoxyethane were calculated and compared with the values of Pilcher and Fletcher.[8] The differences between the calculated and observed values are only 0.04 and 0.21 kcal/mol, respectively, and confirm the accuracy of the computed group increments:

$- \Delta H_f^0(\text{g, dimethoxymethane}) = 51.39 + 2.33 \times 3 + 5.90 \times 2 + 13.365 - 0.15 \times 2 = 83.25$ kcal/mol (obs.[8] 83.21 kcal/mol)

$- \Delta H_f^0(\text{g, 1,1-dimethoxyethane}) = 51.39 + 2.33 \times 4 + 5.53 \times 2 + 5.90 \times 2 + 13.365 - 2.93 - 0.15 \times 2 - 0.765 = 92.94$ kcal/mol (obs.[8] 93.15 kcal/mol).

Pilcher and Fletcher [8] also reported group increments for the estimation of enthalpies of formation of gaseous acetals. However, they did not estimate steric terms (S_{15}^{HH} *etc.*), and hence their value, -3.65 kcal/mol, for the destabilization effect due to an O,C,O-trio attached to the same carbon atom differs greatly from the value computed in this study (Table 2). Moreover, their heats of atomization data for 2,2-dimethoxypropane and 2,2-diethoxy-propane [25] are not in accord with the original values of Stern and Dorer.[25-27] In my opinion, the enthalpy of formation of 2,2-dimethoxypropane, measured by Stern and Dorer,[25] may be considered reliable (Table 1), whereas the value for 2,2-diethoxypropane seems less accurate (Table 3).

5. Enthalpies of formation of orthoesters

The following general equation (Tables 2 and 3) may be written for this series of compounds:

$$-\Delta H_f^0(\text{g, orthoesters}) = 71.70 + 2.33n_c + 2.74n_1 + 5.53n_2 + 5.90n_3 +$$

$$13.365n_4 - 0.62n_5 - 1.32n_6 - 2.94n_7 - 7.42n_8 - 0.765n_9 - 0.15n_{10} - 2.00n_{11} \qquad (6)$$

The most stable rotamer of orthoesters generally has two rabbit-ear effects, and hence the constitution of the destabilization effect due to a non-bonded oxygen trio attached to the same carbon atom will be discussed in detail in a publication on enthalpies of formation of methyl and ethyl orthoformates.[6]

5. Enthalpies of formation and ring strains of cyclic ethers

The enthalpies of formation of gaseous oxirane (I), oxetane (II), tetrahydrofuran (III), and tetrahydropyran (IV) have been determined by Pell and Pilcher.[28]
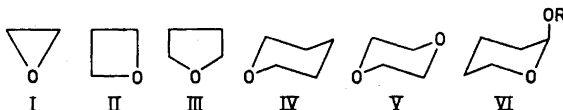
For 1,4-dioxane (V), the value reported by Snelson and Skinner [15] was accepted. Enthalpies of formation are also available for gaseous 2-methoxytetrahydropyran,[11] and 2-(2-methoxyethoxy)tetrahydropyran [5] (VI).

The enthalpies of formation of cyclic "oxanes" may be calculated from the equation:

$$-\Delta H_f^0(\text{g, oxanes}) = \sum E_b(\text{g}) + 2.74n_1 + 5.53n_2 + 5.90n_3 + 13.365n_4 - 0.62n_5 -$$

$$1.32n_6 - 2.94n_7 - 7.42n_8 - 0.765n_9 - 0.15n_{10} - 2.00n_{11} + \qquad (7)$$

$$[RS] - \Delta H_a^0(\text{g, atoms})$$

where [RS] is a term representing the apparent ring strain. The apparent ring strains may be evaluated from the differences between the calculated (eqn. 7) and observed enthalpies of formation. The results for the cyclic ethers mentioned above are shown in Table 5 together with comparative data for corresponding cyclanes.[28] Generally, the apparent ring strains derived from the computed group increments (Table 2 and eqn. 7) are in satisfactory agreement with previous results. As it is based on enthalpies rather than energies, the apparent ring strain contains a systematic error of mRT, where m is the number of rings in the molecule.[29] However, when dealing with unicyclic compounds only, the apparent ring strains are comparable, since all of them include the same systematic error.

Pilcher and Fletcher [8] stated erroneously that the destabilizing effect due to steric requirements in 2-methoxytetrahydropyran is nil, although Pell and Pilcher [28] reported earlier, that even tetrahydropyran has an apparent ring strain of about 1.2 kcal/mol. The contributory group increments and the conformational effects in 2-alkoxytetrahydropyrans have been discussed in detail by Pihlaja and Tuomi.[5]

Table 5. Apparent ring strains in cyclic ethers and in corresponding cyclanes.

Compound	$-\Delta H_f^0(g)$, kcal mol^{-1}		[RS]^a, kcal mol^{-1}	Ref.
	Exptl.	Calc.		
Cyclopropane	-12.73	14.95	27.68^b	28, 13
			27.43	28
Oxirane	12.58	39.54	26.96	28
			27.28	28
Cyclobutane	-6.44	19.93	26.37^b	28, 13
			26.04	28
Oxetane	19.25	44.60	25.35	28
			25.51	28
Cyclopentane	18.45	24.92	6.46^b	28, 13
			6.05	28
Tetrahydrofuran	44.03	49.67	5.64	28
			5.63	28
Cyclohexane	29.43	29.89	0.46^b	28, 13
			-0.02	28
Tetrahydropyran	53.40	54.74	1.34	28
			1.16	28, 7
1,4-Dioxane	75.95	79.07	3.12	15
			3.79	7
2-Methoxytetra-hydropyran	95.5	96.00^c	0.50	11, 5
			0	8
2-(2-Methoxyethoxy)-tetrahydropyran	134.6	135.54^c	0.94	5

^{a} ΔH_f^0(g, exptl.) $-\Delta H_f^0$(g, calc.). ^{b} Derived from group increments of Kalb *et al.*[13] for alkanes.
^{c} Calculated for the axial conformers in which rabbit-ear effects do not exist. See also Ref. 3.

Månsson reported the value -97.50 kcal/mol for the enthalpy of formation of 3,6-dioxaoctane, for which the value -99.32 kcal/mol may be derived, using the computed bond-bond interaction scheme. Månsson stated that the difference 1.82 kcal/mol is due to an excess interaction between the 1,4-oxygen atoms. She also assumed that the apparent ring strain of 1,4-dioxane is the sum of the [RS] in tetrahydropyran (1.34 kcal/mol) and the above value for the interaction between 1,4-oxygen atoms (1.82 kcal/mol), which is in good agreement with the value 3.12 kcal/mol computed for 1,4-dioxane (Table 5). However, 2-(2-methoxyethoxy)tetrahydropyran has an [RS] term of only about 1 kcal/mol [6] although it includes also a pair of 1,4-oxygen atoms. Hence, it seems probable, that the apparent ring strain in 1,4-dioxane is twice as great as in tetrahydropyran (*i.e.* 2.7 kcal/mol). More work with compounds containing 1,4-oxygen atoms is required for correct conclusions.

Generally, the apparent ring strain is slightly reduced when a methylene group is replaced by an oxygen atom, except in the six-membered rings in which the strain is somewhat increased (Table 5).

6. Enthalpies of formation and ring strains of cyclic acetals

Pihlaja and Heikkilä,[30] and Luoma [10] measured enthalpies of formation of 1,3-dioxane and several of its methyl derivatives. Skuratov *et al.*[11] reported

these quantities for 1,3-dioxane, 4-methyl-1,3-dioxane, 1,3-dioxaheptane and 1,3-dioxaoctane. Recently, Pihlaja and Heikkilä [9] reported the enthalpies of formation of some 1,3-dioxolanes. Several authors have measured the value of $-\Delta H_f^0(s)$ of trioxane,[31-35] and Månsson [31] has reported the enthalpy of formation of solid tetroxane, and the enthalpies of sublimation for trioxane and tetroxane. The enthalpy of formation of gaseous cis-2,4,6-trimethyl-1,3,5-trioxane has been reported by three groups of authors.[4,36,37] The results are collected in Table 6. When not available, the enthalpies of vaporization were estimated by the method of Wadsö.[21]

Table 6. Apparent ring strains in cyclic acetals and in corresponding cyclanes.

| Compound | $-\Delta H_f^0(g)$, kcal mol^{-1} | | [RS]^a, kcal mol^{-1} | Ref. |
	Exptl.	Calc.		
Cyclopentane	18.45	24.91	6.46^b	28
1,3-Dioxolane	72.10	79.04	6.94^c	9
2-Methyl-1,3-dioxolane	84.14	89.51	5.37^c	9
cis-2,4-Dimethyl-1,3-dioxolane	91.45	98.01	6.56^c	9
Cyclohexane	29.43	29.89	0.46^b	28
1,3-Dioxane	83.42	84.12	0.70	10, 30
	84.00	84.12	0.12	11
4-Methyl-1,3-dioxane	92.56	93.39	0.83	11
2-Methyl-1,3-dioxane	94.79	94.57	−0.22	10, 30
cis-4,6-Dimethyl-1,3-dioxane	103.29	102.67	−0.62	10
Trioxane	111.32	118.54	7.22	31, 4
			6.13	31
	110.85	118.54	7.69	32, 4
	110.83	118.54	7.71	35, 4
cis-2,4,6-Trimethyl-1,3,5-trioxane	153.06	149.90	−3.16	4
	154.1	149.90	−4.20	36, 4
	154.3	149.90	−4.40	37, 4
Cycloheptane	28.63	34.87	6.24^b	38
1,3-Dioxacycloheptane	82.94	89.19	6.25	11
Cyclooctane	29.81	39.86	10.05^b	38
1,3-Dioxacyclooctane	79.90	94.26	14.36	38
Tetroxane	148.24	158.05	9.81	31

^{a} $\Delta H_f^0(g,$ exptl.$)$ − $\Delta H_f^0(g,$ calc.$)$. ^{b} Derived from group increments of Kalb et al.[13] for alkanes. ^{c} Mean 6.3 kcal mol^{-1}.

The apparent ring strains in the above compounds may again be evaluated by computing $-\Delta H_f^0(g)$ from eqn. (7) and comparing this value with the experimental one (Table 6).

Only data for some of the simplest members of the 1,3-dioxane series are shown in Table 6, since the conformational energies of polysubstituted 1,3-dioxanes are dealt with elsewhere.[10] The apparent ring strain in 1,3-dioxanes is virtually equal to that in cyclohexane, although one rabbit-ear effect exists

in the former compounds.[12] This may, at least partly, be due to the fact that the rabbit-ear interaction is offset by diminished non-bonded hydrogen-hydrogen interactions. Similarly, the apparent ring strain of 1,3-dioxolane and its derivatives (Table 6) is nearly equal to that of cyclopentane. Also the [RS] terms of the larger "oxanes" are nearly equal to the corresponding terms of cyclanes. However, trioxane and cis-2,4,6-trimethyl-substituted trioxane are exceptional. After submission of the preceding paper of this series,[4] Birley and Skinner,[39] and Fletcher and Pilcher [40] reported the value − 25.95 kcal/mol for the enthalpy of formation of gaseous formaldehyde. Busfield and Merigold [4,35] measured the enthalpy change − 46.5 kcal/mol for the reaction

$$3 \ CH_2O \ (g) \longrightarrow \text{trioxane (s)}$$

The above data lead to the value − 124.35 kcal/mol for the enthalpy of formation of solid trioxane, in good agreement with the values of Månsson,[4,31] and Delepiné and Badoche [4,32] (− 124.84 and − 124.37 kcal/mol, respectively). Hence, the most reliable enthalpy of formation value for gaseous trioxane seems to be that of Månsson,[4,31] − 111.32 kcal/mol, which implies a ring strain exceeding 7 kcal/mol (Table 6), whereas those values based on the work of Walker and Carlisle [4,31,33,34] are erroneous.

The anomalous stability of cis-2,4,6-trimethyl-1,3,5-trioxane has been discussed earlier.[4] A possible interpretation may be the great symmetry of the triequatorial system, since, for example, also the biased cis-4,6-dimethyl-1,3-dioxane shows an excess stability of about 1.4 kcal/mol (Table 6) when compared with the apparent ring strain of 1,3-dioxane. Assuming that a similar excess stability prevails in cis-2,4,6-trimethyl-1,3,5-trioxane per a pair of equatorial methyl groups, it should be more stable than the parent compound by about 3 − 4 kcal/mol, still in poor agreement with the observed value 10.4 kcal/mol (Table 6). On the basis of the above discussion it is probable that cis-2,4,6-trimethyl-1,3-dioxane also has excess stabilization, but, unfortunately, its enthalpy of formation has not been measured.

In this context it may be mentioned that Benson et al.[27] derived additivity rules for the estimation of enthalpies of formation of several types of compounds. However, their values for the apparent ring strains of the above "oxanes" deviate greatly from the values derived in this work. Moreover, they accepted the value − 120.8 kcal/mol for the enthalpy of formation of gaseous trioxane at 25°C,[31] which is based erroneously on the enthalpy of vaporization at its boiling point. Nevertheless, they used this erroneous result to estimate the group contribution of $C - (N)_2 - (H)_2$.

CONCLUSIONS

An Allen-type bond-bond interaction scheme, derived for aliphatic acyclic alcohols, ethers, acetals, and orthoesters, has been successfully employed to estimate ring strains in several "oxanes". The equations derived for the direct calculation of the enthalpies of formation of acyclic alcohols, ethers, acetals, and orthoesters yield quite reliable results as shown by the excellent agree-

ment between the calculated and experimental values for dimethoxymethane and 1,1-dimethoxyethane.

The results show also that extension of the scheme to alkanes and their oxygen analogs may well be possible by performing further computations. However, the $-\Delta H_f{}^0(g)$ values for some higher alkanols and acetals require re-examination and also the effect of 1,4-oxygen atoms seems to be worth additional work. The most curious effects were found in trioxanes and point to the need for further investigations.

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