δ 6.8 (broad), 4.33 (triplet), and 2.72 (triplet); the relative intensities were 1:1:1. UV absorption (MeOH) was found at 256 mμ (log ε 4.00).

2-Amino-3-cyano-5,6-dihydro-4H-pyran (II).
Sodium (7.8 g) and malononitrile (22 g) gave with 3-bromopropanol (47 g) under the same conditions colourless crystals (21 g, 51 %), m.p. 107−108°. (Found: C 58.31; H 6.47; N 22.36. Calc. for $C_6H_8N_2O$: C 58.05; H 6.50; N 22.57). IR absorptions were located at 3450, 3350, 2175, 1630, and 1580 cm⁻¹, NMR (DMSO-d_6) signals at δ 6.0 (broad), 4.08 (triplet), 2.12 (triplet), and 1.8 (quintet) with relative intensities 1:1:1:1, and UV absorption at 254 mμ (log ε 3.83).

α-Cyano-γ-butyrolactone (III). A solution of 2-amino-3-cyano-4,5-dihydrofuran (I) (3.5 g) in 1 N sulphuric acid (60 ml) was kept at room temperature for 30 min. During this period it was extracted with ether at short intervals. The combined ether extracts were dried with sodium sulphate, and the solvent evaporated under reduced pressure. Distillation of the residue gave the lactone (1.4 g, 40 %), b.p.$_{10}$ 169−172°. The NMR and IR spectra were identical with those of an authentic sample, prepared by a different method.[4]

α-Cyano-δ-valerolactone (IV). Hydrolysis of 2-amino-3-cyano-5,6-dihydro-4H-pyran (II) (6 g) in 1 N sulphuric acid (100 ml) under the same conditions, afforded a colourless liquid (3.5 g, 55 %), b.p.$_{0.07}$ 128−130°, which crystallised within a few minutes, m.p. 51−52°. (Found: C 57.44; H 5.72; N 10.58. Calc. for $C_6H_7NO_2$: C 57.59; H 5.64; N 11.20). IR absorptions (KBr) were found at 2250 and 1730 cm⁻¹. NMR signals (CDCl$_3$) were located at δ 4.45 (triplet), 3.75 (four lines), and about 2.2 (multiplet); the relative intensities were 2:1:4. These data are consistent with the structure (IV).

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Bond-Bond Interactions in Organic Oxygen Compounds

Part III. Enthalpy of Formation of 2-(2-Methoxyethoxy)tetrahydropyran and the Contributory Group Increments

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2-(2-Methoxyethoxy)tetrahydropyran (I) is a very suitable compound for a study of bond-bond interactions [1,2] since several increments including those due to oxygen atoms are involved.
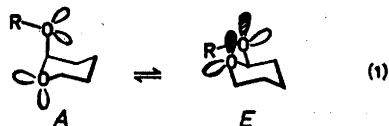
$$\text{I} \quad R = CH_3OCH_2CH_2-$$
$$\text{II} \quad R = CH_3O-$$

One rabbit-ear effect [3−6] and one methyl-oxygen *gauche* interaction exist in the most stable rotamer of the equatorial conformer of 2-alkoxytetrahydropyrans (eqn. 1; E). Similarly, the most stable rotamer of the axial conformer (eqn. 1; A) is that in which two 1,3-diaxial hydrogen-oxygen interactions and one methyl-oxygen *gauche* interaction contribute.[6] The enthalpy difference between IA and IE (eqn. 1) is hence nearly equal to the difference between the enthalpy of inter-action due to one rabbit-ear effect and that due to one axial alkoxy group. The latter interaction is obviously slightly greater than in methoxycyclohexane where $\Delta G°$ is 0.4 kcal/mole in favor of the equatorial conformation.[7] de Hoog and coworkers [8] have reported that the enthalpy difference between axial and equatorial conformers of 2-alkoxytetrahydropyrans is about 1.05 kcal/mole. If it is assumed that $\Delta H°$ for an axial alkoxy group in position 2 of tetrahydropyran is about 0.7 kcal/mole,

Table 1. Combustion data for 2-(2-methoxyethoxy)tetrahydropyran (I).

$t_h = t_i = 25.00°C$
$e^c(\text{calor}) = 1360.17 \pm 0.21$ cal/°F $-\Delta e_c°(\text{gel}) = 4562.39 \pm 4.93$ cal/g
$M = 160.21$

m g	m' g	Δt °F	ΔE_{ign} cal	$\Delta E_{dec}{}^t$ (HNO$_3$) cal	$\Delta E_{dec}{}^t$ (H$_2$SO$_4$) cal	$\Delta E\Sigma$ cal	$e^f(\text{cont})$ cal/°F	$-\Delta U_c°/M$ cal/g
0.751134	0.12654	4.399	18.52	11.61	0.99	2.74	2.39	7166.09
0.742975	0.12366	4.349	12.52	10.685	0.97	2.70	2.39	7180.20
0.759257	0.11357	4.397	20.36	10.96	0.89	2.72	2.39	7162.41
0.759573	0.12499	4.431	12.35	10.87	0.98	2.77	2.40	7162.29
0.749022	0.12027	4.370	15.90	11.26	0.945	2.71	2.39	7175.83
0.752445	0.11713	4.365	5.24	8.58	0.92	2.69	2.39	7170.96
0.746500	0.12948	4.379	16.13	9.48	1.02	2.75	2.39	7162.16

[a] Standard deviation of the mean.
[b] Overall standard deviation.[12]
[c] Twice the overall standard deviation.[12]

$-\Delta U_c°/M = 7168.56 \pm 2.75^a$ cal/g
$-\Delta U_c°(l) = 1148.48 \pm 0.51^b$ kcal/mole
$-\Delta H_c°(l) = 1149.96 \pm 1.01^c$ — » —
$-\Delta H_f°(l) = 148.98 \pm 1.01$ — » —

the interaction energy of a rabbit-ear effect should be around 1.7 kcal/mole.

The above data make it possible to consider the influence of anomeric effects on the enthalpies of formation of 2-alkoxy-tetrahydropyrans and this is why the enthalpy of formation of 2-(2-methoxy-ethoxy)tetrahydropyran (I) was determined.

2-(2-Methoxyethoxy)tetrahydropyran was kindly donated by Mr. Kari Miikki, Ph.M. It was distilled several times from metallic sodium after which gas chromatographic analysis using a Perkin-Elmer F 11 gas chromatograph, equipped with a column containing 10 % potassium hydroxide on Apiezon L, showed no impurities. B.p. 198.3°C/760 torr, 75°C/11 torr,[6] $n_d{}^{20}$ 1.4373,[6] and $d_4{}^{20}$ 1.0026.[6]

The combustion experiments and calculations were carried out as described earlier.[9-12] The heat of combustion of the gelatine capsules (4562.4 ± 4.9 cal/g) was determined and the calorimeter (Parr Instruments and Co.) was calibrated as described previously.[11] The combustion data for 2-(2-methoxyethoxy)-tetrahydropyran (I) are presented in Table 1.

Using the bond-bond interaction scheme presented by Pihlaja and Kankare[1,2] we can compute the enthalpy of formation for IA (eqn. 1) in the gaseous state:

$-\Delta H_f°(\text{g,IA}) = \Sigma E_b + 3\Gamma_{CCC} + 5\Gamma_{CCO} + \Gamma_{OCO} + 3\Gamma_{COC} + \Delta_{OCO} + [RS] + S_{15}{}^{HO:} - \Delta H°$
(axial OR) $- \Delta H_a°(\text{atoms})$ (2a)

ΣE_b is the sum of bond energies,[1] Γ_{CCC}, Γ_{CCO}, Γ_{OCO}, and Γ_{COC} are group increments due to pairs of next-nearest-neighbor carbon atoms, carbon and oxygen atoms and oxygen atoms connected by a carbon atom, and carbon atoms connected by an oxygen atom, respectively[1,2] (Table 2). Δ_{OCO} is an increment caused by an

Table 2. Values of the group increments contributing to the heats of formation of gaseous 2-alkoxytetrahydropyrans I and II (eqn. 1).

Group increment	Contributory energy to $-\Delta H_f°(\text{g})$ kcal/mole	Ref.
Γ_{CCC}	2.74	1,2
Γ_{CCO}	5.51	1,2
Γ_{COC}	5.92	1,2
Γ_{OCO}	13.29	1,2
Δ_{OCO}	−2.93	1,2
$S_{15}{}^{HO:}$	−0.12	1,2
[RS]	−1.4	2,13

O,C,O-trio attached to the same carbon atom and [RS] an increment correcting for the effect of the apparent ring strain [2,13] (Table 2). $S_{15}^{HO:}$ is equal to the interaction between the ring oxygen and an α-methylene proton of the alkoxy group [1,2] (Table 2). $\Delta H_a{}^\circ$(atoms) is the sum of the heats of atomization of the elements.[1] By substituting the values given in Table 2 and Refs. 1 and 2 into eqn. (2a), we obtain:

$$-\Delta H_f{}^\circ(g,\ IA) = 2451.72 + 62.52 - 0.7 -$$

$$2379.32 = 134.2\ kcal/mole \qquad (2b)$$

In order to compare this computed value with the value of $-\Delta H_f{}^\circ$ (liq., I) determined in this work, the heat of vaporization at 25°C for 2-(2-methoxyethoxy)tetrahydropyran (I) must be evaluated. Wadsö[14] reported equation

$$\Delta H_{vap}(25°C) = 5.0 + 0.041 t_{bp} \qquad (3)$$

for this quantity, but for compounds boiling above 170°C this is only an approximate expression. When some known deviations[14] are taken into account, the value 14.4 ± 0.5 kcal/mole is proposed for the heat of vaporization of I at 25°C. The enthalpy of liquid I is -149.0 ± 1.0 kcal/mole and thus $-\Delta H_f{}^\circ(g,\ I) = 134.6 \pm 1.5$ kcal/mole. This value is in reasonable agreement with the value 134.2 kcal/mole calculated for the axial conformer of I (eqn. 2b). Thus 2-(2-methoxyethoxy)tetrahydropyran exists predominantly in the axial conformation (IA), in agreement with the conclusion of other authors.[3-6,8]

Skuratov et al.[15] reported the value −868.8 kcal/mole for the heat of combustion of 2-methoxytetrahydropyran (II; b.p. 125°C) at 20°C. Skuratov's value may be corrected from 20 to 25°C using the value C_p (tetrahydropyran, liq.) = 37.4 cal/degree·mole,[13] after which the value −105.6 kcal/mole is obtained for the enthalpy of formation of II in the liquid state at 25°C. By computing ΔH_{vap} from eqn. (3), the value −95.5 kcal/mole is derived for the enthalpy of formation of 2-methoxytetrahydropyran (II) in the gaseous state.

Using the scheme shown in eqn. (2a), we find (eqn. 4; Table 2):

$$-\Delta H_f{}^\circ(g,\ IIA) = \Sigma E_b + 3\Gamma_{CCC} + 3\Gamma_{CCO} +$$

$$\Gamma_{OCO} + 2\Gamma_{COC} + \Delta_{OCO} + [RS] + S_{15}^{HO:} - \Delta H^\circ$$

$$(axial\ OR) - \Delta H_a{}^\circ(atoms)$$

$$= 1819.42 + 45.58 - 0.7 - 1769.60$$

$$= 94.7\ kcal/mole \qquad (4)$$

The agreement between the calculated and observed value is again satisfactory showing that the result of Skuratov and coworkers[15] is quite reliable.

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