

281. *Heats of Combustion and Molecular Structure. Part V.¹ The Mean Bond Energy Term for the C-O Bond in Ethers, and the Structures of Some Cyclic Ethers.*

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The mean bond energy term for the C-O bond in ethers has been reconsidered in conjunction with combustion data on tetrahydropyran and used in a molecular structural analysis of combustion data on cyclic ethers and on diphenyl ether.

A SUITABLE starting point for the study, by combustion, of the molecular energetics of organic compounds containing carbon, hydrogen, and oxygen appeared to be the mean bond energy term, $\bar{E}(\text{C-O})$, in ethers. By studying combustion data on simple ethers and obtaining experimental results for tetrahydropyran we obtained a reasonable value, and applied it to the molecular structural analysis of the experimentally determined heats of combustion of the cyclic ethers dihydropyran, tetrahydrofuran, dibenzopyran, and dibenzofuran, and of diphenyl ether.

EXPERIMENTAL

Preparation and Purification of Materials.—Some microanalyses are by Mr. W. Morton (University of Manchester).

Benzoic acid. B.D.H. Thermochemical Standard was used.

Tetrahydropyran (Kodak Ltd.) was refluxed over sodium and distilled, the fraction, b. p. 86.9—87.1°/744 mm. (Clark ² gives b. p. 88.0°/760 mm.) being used for combustion ($n_D^{19.6}$ 1.4198; Skuratov ³ gives n_D^{20} 1.4212 and Heilbron and Bunbury ⁴ give $n_D^{18.5}$ 1.4195) (Found: C, 69.86; H, 11.66. Calc. for C₅H₁₀O: C, 69.72; H, 11.70%).

Dihydropyran (I.C.I.) was partially dried with anhydrous sodium carbonate, then fractionated, the fraction, b. p. 84—85°, being collected. It was dried by prolonged refluxing with sodium until it no longer evolved hydrogen when brought into contact with a freshly prepared sodium surface (for the difficulty of drying dihydropyran, see Sawyer and Andrus ⁵). Most of the dihydropyran so dried distilled at 84.4°/742 mm. (Sawyer and Andrus ⁵ give 84—86°) (Found: C, 71.4; H, 9.5. Calc. for C₅H₈O: C, 71.4; H, 9.5%).

Tetrahydrofuran (I.C.I.) was dried (CaH₂) and fractionated from phosphoric oxide through a Fenske column. The product, b. p. 64.0—66.2°, was collected, refluxed over sodium for 1 hr., and again fractionated. It distilled almost completely at 66.0°/768 mm. (Starr and Hixon ⁶ give b. p. 64—66°/760 mm.) (Found: C, 66.5; H, 10.9. Calc. for C₄H₈O: C, 66.7; H, 11.1%).

Diphenyl ether (British Scherring Research Institute) was twice recrystallised from 90% ethanol and was further purified by fractional freezing twice, by the method described by Schwab and Wichers ⁷ for the purification of benzoic acid. The product, m. p. 27.2° (Timmermans ⁸ gives 26.9°) was powdered in an agate mortar and stored over phosphoric oxide.

Dibenzopyran (L. Light and Co., Ltd.) was recrystallised four times from 95% ethanol, m. p. 100.4—100.5° (Ipatiev, Orlov, and Petrov ⁹ give m. p. 100.5°).

¹ Part IV, Cass, Fletcher, Mortimer, Quincey, and Springall, *J.*, 1958, 958.

² Clarke, *J.*, 1912, **101**, 1802.

³ Skuratov, Moscow University, personal communication.

⁴ Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1946.

⁵ Sawyer and Andrus, *Organic Syntheses*, Coll. Vol. 3, p. 276.

⁶ Starr and Hixon, *Organic Syntheses*, Coll. vol., **2**, p. 566.

⁷ Schwab and Wichers, *J. Res. Nat. Bur. Stand.*, 1940, **25**, 747.

⁸ Timmermans, "Physico-chemical Constants of Pure Organic Compounds," Elsevier, Brussels, 1950.

⁹ Ipatiev, Orlov, and Petrov, *Ber.*, 1927, **60**, 130.

Dibenzofuran (L. Light and Co., Ltd.) was dissolved in ether and shaken with two successive portions of aqueous sodium hydroxide (2M). The ether solution was then washed with water, separated, and dried (MgSO₄). The solvent was evaporated off and the dibenzofuran was twice recrystallised from 80% ethanol and dried *in vacuo*. The colourless product had m. p. 81.9–82° (Cullinane and Plummer¹⁰ give m. p. 82.4°) (Found: C, 85.8; H, 4.8. Calc. for C₂H₈O: C, 85.7; H, 4.8%).

Vapour-pressure Measurements.—Accurate vapour-pressure data were available only for diphenyl ether and tetrahydrofuran. The vapour pressures of the other compounds were measured in an apparatus of the type described by Sanderson.¹¹ The values of *A* and *B* of the equation $\log_{10} p$ (mm.) = *A*/*T* + *B* are given in Table 1, together with those for the two compounds previously investigated. The derived latent heats of vaporisation (liquid to vapour), given by $L_v = -4.56A \times 10^{-3}$ kcal./mole, are also listed.

TABLE 1. *Latent heats.**

Compound	- <i>A</i>	<i>B</i>	Temp. range	<i>L_v</i> (kcal./mole)
Tetrahydropyran	1825.35	7.99	0–15°	8.35
Dihydropyran	1680.98	7.57	0–15	7.7
Tetrahydrofuran ^a	1660.5	7.80	20–60	7.6
Diphenyl ether ^b	3351.9	9.58	40–60	15.2
Dibenzopyran	4632.4	11.58	140–160	21.2
Dibenzofuran	3457.6	9.38	130–145	15.8

* For compounds burnt as solids, the latent heat of fusion was assumed to be 4 kcal./mole (Walden, *Z. Elektrochem.*, 1908, **14**, 713) and is added to the *L_v* term to give the latent heat of sublimation, *L_g*st.

^a Klages and Mohler, *Ber.*, 1948, **81**, 411. ^b Bent and Francel, *J. Amer. Chem. Soc.*, 1948, **70**, 634.

TABLE 2. *Tetrahydropyran (M, 86.13).*

Wt. taken, * <i>m</i>	CO ₂ (obs. : calc.)	Δ <i>R</i> (ohms)	Corrections (cal.)			<i>C</i> (cal./ohm)	–Δ <i>U_b</i> † (kcal./mole)
(g.)		(fuse)	(HNO ₃)	(carbon)			
0.2699	1.0010	0.06088	24.9	0.7	—	2.8	751.6
0.3954	1.0009	0.08892	24.1	1.3	—	4.1	751.1
0.4208	1.0020	0.09468	17.2	1.0	—	4.4	751.0
0.3320	1.0012	0.07472	22.8	1.4	7.8	3.5	752.9

* Weight *in vacuo*.

† –Δ*U_b* = 10⁻³ *M/m* [(*E* + *C*)Δ*R* – Corr. (fuse + HNO₃ – carbon)] kcal./mole.

Combustion Calorimetry.—Tetrahydropyran was burnt in a twin-valve Parr bomb (energy equivalent, *E* = 39,058 ± 20 cal./ohm) as described in Part IV.¹ The results are given in Tables 2 and 4. In only one case was carbon found in the bomb after combustion. It was weighed and a correction of 7.84 kcal./g. was applied. The carbon dioxide formed on combustion varied from the calculated quantity to 0.20% above it (the experimental error of analysis is approximately ±0.05%), probably owing to very slight contamination by dihydropyran from which the tetrahydropyran was prepared, the b. p.s of the two compounds being only 3° apart. (The high carbon and low hydrogen contents found in the microanalysis of tetrahydropyran are compatible with this.) The experimental error ascribed to –Δ*U_b* and –Δ*H_c*^o of ±0.9 kcal./mole has been increased to ±1.5 kcal./mole to include the uncertainty due to the slight impurity.

The –Δ*U_b* terms were converted into –Δ*H_c*^o terms, the standard heat of combustion, by use of the expression

$$-\Delta H_c^o = -\Delta U_b - w - \Delta nRT,$$

where *w* is the Washburn correction, calculated according to Prosen,¹² and Δ*n* is the increase in the number of molecules of gas in the combustion reaction.

Slightly lower values of –Δ*H_c*^o for tetrahydropyran have been reported by Dr. G. R. Nicholson (Imperial Chemical Industries Limited, Blackley), 749.0 kcal./mole,¹³ and Professor

¹⁰ Cullinane and Plummer, *J.*, 1938, 63.

¹¹ Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 48.

¹² Prosen, "Experimental Thermochemistry," ed. Rossini, Interscience, New York, 1956.

¹³ Nicholson, personal communication.

S. M. Skuratov and his co-workers (Moscow), 750.1 ± 0.2 kcal./mole.¹⁴ We thank Dr. Nicholson and Professor Skuratov for discussions which lead us to feel that any significant discrepancies between their values and ours are probably due to undetected contamination of their specimens by dihydropyran.

The remaining combustions were made in a Mahler-Cook stainless-steel bomb. The energy equivalent of the calorimeter system, E' , was $3085.5 \pm 24.18\theta_m$ cal./deg., where θ_m is a mean temperature, as defined in Part I.¹⁵ The apparatus, experimental procedure, and method of calculation were fully described in Part I.¹⁵ Diphenyl ether, dibenzofuran, and dibenzopyran were burnt as solids, and the remainder as liquids in glass ampoules. The results are recorded in Tables 3 and 4.

TABLE 3.

Wt. taken, <i>m</i> (g.) *	$\Delta\theta$ (° C)	θ_m (° C)	Corrections (cal.)			E' (cal./deg.)	C (cal./deg.)	$-\Delta U_b \dagger$ (kcal./mole)
			(fuse)	(HNO ₃)	(carbon)			
Dihydropyran (<i>M</i> , 84.11)								
0.7907	2.0950	4.69	71.8	2.2	0.8	3198.0	0.7	705.6
0.8252	2.1847	4.65	71.8	2.5	3.2	3197.0	0.7	705.3
0.9749	2.5624	4.78	31.9	2.8	1.6	3200.5	0.8	705.3
0.9080	2.3885	4.53	31.9	2.8	3.9	3195.0	0.8	704.8
0.8336	2.2083	4.61	71.8	2.7	2.2	3196.5	0.8	705.6
Tetrahydrofuran (<i>M</i> , 72.10)								
0.8654	2.2785	4.22	71.8	1.7	4.8	3187.0	0.8	599.4
0.9716	2.5359	4.66	71.8	2.4	5.2	3198.0	1.0	596.9
0.9771	2.5569	4.57	71.8	3.1	3.6	3196.0	1.0	597.9
0.9906	2.5999	4.26	71.8	2.9	6.4	3188.0	1.0	598.5
Diphenyl ether (<i>M</i> , 170.20)								
0.7974	2.1391	4.75	4.0	1.8	1.6	3199.0	0.5	1459.9
0.8126	2.1813	4.68	4.0	0.8	0.8	3197.5	0.5	1460.2
0.8036	2.1644	4.36	4.0	0.7	3.9	3190.5	0.5	1462.6
Dibenzopyran (<i>M</i> , 182.21)								
0.8612	2.3133	4.44	71.8	2.8	1.6	3192.0	0.5	1547.0
0.8724	2.3439	4.52	71.8	3.0	0.8	3194.0	0.5	1548.4
0.8937	2.4013	4.56	71.8	2.0	1.2	3195.0	0.5	1549.6
0.8979	2.4150	4.46	71.8	2.2	2.4	3192.5	0.5	1550.2
Dibenzofuran (<i>M</i> , 168.18)								
0.8223	2.1717	4.31	71.8	1.1	2.3	3189.0	0.4	1402.2
0.8826	2.3240	4.31	71.8	1.7	1.9	3189.0	0.5	1398.8
0.9040	2.3784	4.62	71.8	2.2	1.6	3196.0	0.5	1400.9

* Weight *in vacuo*.

† Where $-\Delta U_b = 10^{-3} M/m [(E' + C) \Delta\theta - \text{corr. (fuse + HNO}_3 - \text{carbon)}]$ kcal./mole.
For symbols see Part I.¹⁵

TABLE 4.

Compound	$-\Delta U_b$ mean (kcal./mole)	Standard deviation ($-\Delta U_b$) (%)	Overall standard deviation (%)	Washburn corr., <i>w</i> (kcal./mole)	ΔnRT (kcal./mole)	ΔH_c° (kcal./mole)
Tetrahydropyran ...	751.9	0.120	0.160	0.30	-1.2	752.8 ± 1.5
Dihydropyran	705.3	0.020	0.032	0.35	-0.9	705.9 ± 0.3
Tetrahydrofuran	598.2	0.085	0.089	0.26	-0.9	598.8 ± 0.5
Diphenyl ether	1460.9	0.058	0.063	0.95	-1.2	1461.1 ± 0.9
Dibenzopyran	1548.8	0.045	0.052	1.05	-1.2	1549.0 ± 0.9
Dibenzofuran	1400.6	0.062	0.067	1.0	-0.9	1400.5 ± 1.0

DISCUSSION

Derivation of the Mean Bond Energy Term $\bar{E}(\text{C-O})$ in Ethers.—The only available experimental data on the heats of combustion of simple ethers were found in the classical work of Berthelot and of Thomsen (*circa.* 1890) and are considered in the compilations of Kharasch¹⁶

¹⁴ Skuratov, Kozina, Shteher, and Varushyenko, I.U.P.A.C. Thermochemical Bulletin, 1957, No. 3.

¹⁵ Springall, White, and Cass, *Trans. Faraday Soc.*, 1954, **50**, 815.

¹⁶ Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359.

and, to some extent, of Bichowsky and Rossini.¹⁷ The three simplest ethers, dimethyl,¹⁸ ethyl methyl,¹⁸ and diethyl,¹⁹ were investigated in the gas phase by flame calorimetry. The heats of combustion found, listed in Table 5, have been the basis of all previous estimates of $\bar{E}(\text{C-O})$ in ethers (*e.g.*, Pauling²⁰), special weight being attached to the data on dimethyl ether.* These data have been analysed afresh by use of the methods and auxiliary thermochemical data (heats of formation of carbon dioxide and water, heats of atomisation of elements, and other mean bond energy terms) discussed in earlier Parts^{1, 15, 21, 22} [$-\Delta H_{\text{f}}^{\circ}$ terms: CO_2 , 94.05, H_2O , 68.32. ΔH_{a} terms: C, 171.7; H, 52.09; O, 58.98. $\bar{E}(\text{b})$ terms: C-C, 83.1; C-H, 98.85 kcal./mole]. The derived heats of formation of the gaseous compounds, $-\Delta H_{\text{f},\text{g}}^{\text{st}}$, atomic heats of formation, $-\Delta H_{\text{f},\text{g}}^{\text{a}}$, and individual $\bar{E}(\text{C-O})$ terms are given in Table 5.

We felt it desirable to have an experimental link between this classical work and our own and therefore selected tetrahydropyran as a suitable ether for a new determination. This compound is reasonably accessible, not unduly volatile, and has a structure unlikely to be complicated by strain (see, for example, the dipole-moment studies of H. de Vries Robles²³). $-\Delta H_{\text{c},\text{g}}$ for this compound, and the derived $-\Delta H_{\text{f},\text{g}}$, $-\Delta H_{\text{f},\text{g}}^{\text{a}}$, and $\bar{E}(\text{C-O})$ terms are listed in Table 5.

TABLE 5.
(Energy terms in kcal./mole)

Compound	$-\Delta H_{\text{c},\text{g}}$	$-\Delta H_{\text{f},\text{g}}^{\text{st}}$	$-\Delta H_{\text{f},\text{g}}^{\text{a}}$	$\bar{E}(\text{C-O})$
Dimethyl ether	347.6	45.5	760.5	83.9
Ethyl methyl ether	503.4	52.1	1043.0	84.6
Diethyl ether	660.4	57.7	1324.5	84.8
Tetrahydropyran	761.2 *	50.7	1489.2	84.2

* Given by $-\Delta H_{\text{c},\text{g}} = -\Delta H_{\text{c}}^{\circ} + L_{\text{v}}$.

The agreement between the values $\bar{E}(\text{C-O})$ derived from the classical data and from our own work is gratifying and seems to justify the use of the average of these four estimations, 84.3 kcal./mole, as a reasonable value for $\bar{E}(\text{C-O})$ in ethers [Coates and Sutton²⁴ have established $\bar{E}(\text{C-O})$ in alcohols as 85.5 kcal./mole].

Molecular Energetics of the Cyclic Ethers and of Diphenyl Ether.—The previous approach¹⁵ was followed. For each compound the following calculations were made. (i) $-\Delta H_{\text{f},\text{g}}^{\text{a}}$ was evaluated from the experimental $-\Delta H_{\text{c}}^{\circ}$ and L_{g}^{st} or L_{v} terms. (ii) The mean bond energy terms for all the bonds in the molecule were summed, $\sum \bar{E}(\text{b})$. (iii) The difference $-\Delta H_{\text{f},\text{g}}^{\text{a}} - \sum \bar{E}(\text{b}) = \Delta E$ was evaluated. This quantity, ΔE , indicates molecular stabilisation when positive; molecular strain when negative. These data are given in Table 6.

TABLE 6.
(Energy terms in kcal./mole)

Compound	$-\Delta H_{\text{f},\text{g}}^{\text{a}}$	$\sum \bar{E}(\text{b})$	ΔE	Compound	$-\Delta H_{\text{f},\text{g}}^{\text{a}}$	$\sum \bar{E}(\text{b})$	ΔE
Dihydropyran	1364.4	1356.9	7.5	Diphenyl ether	2628.4	2544.9	83.5
Tetrahydrofuran	1205.8	1208.7	-2.9	Dibenzopyran	2802.3	2711.1	91.2
				Dibenzofuran	2517.9	2430.3	87.6

Dihydropyran (I) shows a stabilisation energy of 7.5 kcal./mole, probably owing to resonance involving the ionic form (II).

Tetrahydrofuran shows a destabilisation (strain) energy of 2.9 kcal./mole, whereas the strain energy of cyclopentane is about 6 kcal./mole. In the latter case, where the bond angles

* Possibly because the Bichowsky-Rossini compilation only deals with organic compounds up to C_2 .

¹⁷ Bichowski and Rossini, "The Thermochemistry of the Chemical Substances," Reinhold, New York, 1936.

¹⁸ Thomsen, "Systematische durchsührung Thermochemischer Untersuchungen," Enke, Stuttgart, 1906, p. 343.

¹⁹ Stohmann, *J. prakt. Chem.*, 1887, **35**, 40, 136.

²⁰ Pauling, "The Nature of the Chemical Bond," Oxford Univ. Press, 1950.

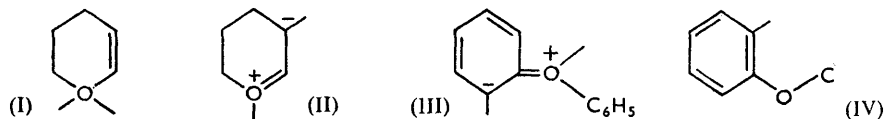
²¹ Cass, Springall, and Quincey, *J.*, 1955, 1188.

²² Springall and White, *J.*, 1954, 2764.

²³ H. de Vries Robles, *Rec. Trav. chim.*, 1940, **59**, 184.

²⁴ Coates and Sutton, *J.*, 1948, 1187.

are almost equal to the normal tetrahedral angle, the strain is attributed to small repulsive forces between hydrogen atoms on adjacent carbon atoms.²⁰ A strain energy slightly less than that of *cyclopentane* is, therefore, to be expected for tetrahydrofuran, owing to the separation of two of the methylene groups by an oxygen atom. The planar model of tetrahydrofuran constructed from electron-diffraction data²⁵ (C-C, 1.34; C-O, 1.43 Å; C-O-C = $111^\circ \pm 2^\circ$) shows only slight strain in the C-C-C angles. For the C-O-C angles, a value of



100° has been allotted by Brie²⁶. From electron-diffraction data, Sutton and Brockway²⁷ give a value of $111^\circ \pm 4^\circ$ for this angle in dimethyl ether. We now suggest a value of $105^\circ \pm 5^\circ$ for the C-O-C angle in dihydrofuran.

Diphenyl ether has a stabilisation (resonance) energy of 83.5 kcal./mole. The value 41.8 kcal. for the fragment C_6H_5-O is in good agreement with the value 41.6 kcal./ C_6H_5-O fragment which can be derived from the reported heats of combustion of methyl phenyl ether and ethyl phenyl ether.²⁸ There is an increase of 2.7 kcal. in the resonance energy for the C_6H_5-O fragment above that of the C_6H_5-C fragment taken as about 38.9 kcal. Moreover, (a) the C-O-C angle in aromatic ethers ($125^\circ \pm 5^\circ$) is larger than that²⁹ in aliphatic ethers ($105^\circ \pm 5^\circ$) and (b) the C-O distance in aromatic ethers (1.36 Å) is shorter than that³⁰ in aliphatic ethers (1.42 Å). These facts all agree with the suggestion³¹ of the occurrence of resonance of the type (III).

Dibenzopyran and dibenzofuran have resonance energies of 91.2 and 87.6 kcal./mole respectively (45.6 and 43.8 kcal./mole for half of the molecule in each compound) compared with 83.5 kcal./mole in diphenyl ether. The stabilisation of the dibenzopyran relative to diphenyl ether, 7.7 kcal., is probably real and may well be due to the increase in molecular rigidity, relative to diphenyl ether, due to the 2 : 2'-methylene bridge, coupled with the angular conditions in the pyran ring system which favour a C-O-C angle of 125° . The whole molecule may be planar, since folding of the molecule along the CH_2-O axis would introduce angular strain particularly at the oxygen atom and also depress the resonance effect, because of the non-planar system (IV) involved. The intermediate position of dibenzofuran is probably due to the fact that though the molecule is constrained to a planar configuration (as suggested by Cullinane and Plummer¹⁰ and Cullinane and Rees³²) so stabilising the ionic oxonium forms, nevertheless the bond angles in the furan section are strained; the C-O-C angle, in particular, is likely to be smaller than 125° .

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²⁵ Beach, *J. Chem. Phys.*, 1941, **9**, 54.

²⁶ Brie, *Anales Soc. españ. fis. quim.*, 1932, **30**, 483.

²⁷ Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473.

²⁸ Badoche, *Bull. Soc. chim. France*, 1941, **8**, 212; May and Springall, unpublished results.

²⁹ Smyth and Walls, *J. Amer. Chem. Soc.*, 1932, **54**, 3230; Maxwell, Hendricks, and Mosely, *J. Chem. Phys.*, 1935, **3**, 699; Coop and Sutton, *J.*, 1938, 1869; Plieth, *Z. Naturforsch.*, 1947, **20**, 409; Leonard and Sutton, *J. Amer. Chem. Soc.*, 1948, **70**, 1564.

³⁰ Hassel and Viervoll, *Acta Chem. Scand.*, 1947, **1**, 149.

³¹ Sutton and Hampson, *Trans. Faraday Soc.*, 1935, **31**, 945.

³² Cullinane and Rees, *Trans. Faraday Soc.*, 1940, **36**, 507.