118. *Heats of Combustion and Molecular Structure. Part VII.*[1] 1 : 3-*Dioxa- and* 1 : 3 : 5-*Trioxa*-cyclo*alkanes.*

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The heats of combustion and latent heats of evaporation of three cyclic ethers, containing the 1 : 3-dioxa-grouping, have been measured. The derived atomic heats of formation have been analysed into mean bond-energy terms. The results indicate that this grouping stabilises the molecules.

In previous Parts the mean bond-energy term for the C–O bond in ethers has been determined [2] and the thermochemistry and structures of some cyclic ethers considered.[1,2] It was during these investigations that the heat of combustion of paraldehyde was reported.[3] It appears that the paraldehyde molecule is more stable than would be expected from the sum of the mean bond-energy terms of the component bonds. This unexpected stabilisation energy is also apparent from data on heats of combustion, although to a smaller extent, in *sym*-trioxan [4] and in the acetals.[5,6]

Elucidation of the problem has been approached by considering the energetics of some di-ethers, with oxygen atoms in both the 1 : 3- and the 1 : 4-positions. The heats of combustion and latent heats of evaporation of 1 : 3-dioxan (I), 5 : 5'-*spiro*bis-1 : 3-dioxan

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[1] Part VI, Cass, Fletcher, Mortimer, Quincey, and Springall, *J.*, 1958, 2595.

[2] Cass, Fletcher, Mortimer, Springall, and White, *J.*, 1958, 1406.

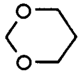
[3] Cass, Springall, and White, *Chem. and Ind.*, 1955, 387.

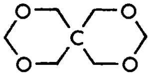
[4] Walker and Carlisle, *Chem. Eng. News*, 1943, **21**, 1251.

[5] Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359.

[6] Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, pp. 89, 95.

(II) and 1 : 3-dioxolan (III) have been measured. Experimental data on paraldehyde (IV) are also recorded.

(I)
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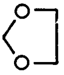

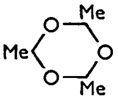

(IV)

EXPERIMENTAL

Preparation of Materials.—" B.D.H. Thermochemical Standard " benzoic acid was used. 5 : 5′-*spiro*Bis-1 : 3-dioxan was prepared by Read's method,[7] and after three crystallisations from ether had m. p. 50·0°, as given by Read.

1 : 3-Dioxan was prepared from trimethylene glycol and methylene sulphate according to Baker's method.[8] It was refluxed over sodium and fractionated; the product had b. p. 104·0—104·5°/746 mm. (Baker gives b. p. 105°/754 mm.).

1 : 3-Dioxolan, prepared from ethylene glycol and methylene sulphate,[8] was refluxed over sodium and fractionated, the fraction collected having b. p. 74·0°/738 mm. (Baker gives b. p. 76°/752 mm.).

Paraldehyde, B.D.H. reagent quality, was dried ($CaCl_2$) and fractionated through an 8 in. column packed with glass helices. The fraction of b. p. 124·5°/767 mm. was collected (Timmermans [9] gives b. p. 124·35°/760 mm.).

Vapour-pressure Measurements.—The vapour pressures of the compounds were measured in an apparatus of the type described by Sanderson.[10] The values A and B of the equation $\log_{10} p(\text{mm.}) = -A/T + B$ are given in Table 1. The derived latent heats of vaporisation (liquid to vapour), given by $L_v = 4{\cdot}57A \times 10^{-3}$ kcal./mole, are also listed. The latent heat of sublimation of 5 : 5′-*spiro*bis-1 : 3-dioxan is assumed to be 4·0 kcal./mole greater than its latent heat of vaporisation.

TABLE 1.

Compound	A	B	L_v (kcal./mole)
5 : 5′-*spiro*Bis-1 : 3-dioxan	2942	7·79	13·4 ± 0·4
1 : 3-Dioxan	1869	6·78	8·5 ± 0·2
1 : 3-Dioxolan	1854	7·21	8·5 ± 0·1
Paraldehyde	2168	7·34	9·9 ± 0·1

Combustion Calorimetry.—The combustions of 5 : 5′-*spiro*bis-1 : 3-dioxan, 1 : 3-dioxan, and 1 : 3-dioxolan were made in the twin-valve bomb (The Parr Instrument Co., Moline, Illinois, U.S.A.) described in Part IV.[11] Temperature changes were recorded by a platinum resistance thermometer and the energy equivalent, E, of the calorimeter was determined by burning benzoic acid pellets. The products of combustion were analysed for carbon dioxide [12] with an accuracy of ±0·05% and in most cases the weight of carbon dioxide was less than that calculated for complete combustion by amounts varying from 0·3 to 0·6%. In no case was carbon found in the bomb after combustion and it was assumed that the discrepancy was due to unburnt ether or traces of water. The results are recorded in Table 2.

After the combustion of 5 : 5′-*spiro*bis-1 : 3-dioxan the calorimeter system was modified as follows. The original solid Baekelite lid to the calorimeter jacket, carrying a reciprocating stirrer, was replaced by a hollow copper lid, through which passes the circulating water, at 28·000 ± 0·005° c, from the calorimeter jacket. This new copper lid carries two counter-rotating propeller stirrers made of twisted brass sheet.

Paraldehyde was burnt in a Mahler–Cook stainless-steel bomb, temperature changes being recorded by a Beckmann thermometer, according to the procedure described in Part I.[13] The energy equivalent of the calorimeter system, E', was $308{\cdot}5 + 24{\cdot}18\theta_m$ cal./deg., where θ_m is a mean temperature as defined in Part I. Combustions were made on three different specimens

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[7] Read, *J.*, 1912, **101**, 2093.

[8] Baker, *J.*, 1931, 1765.

[9] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Brussels, 1950.

[10] Sanderson, " Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 48.

[11] Cass, Fletcher, Mortimer, Quincey, and Springall, *J.*, 1958, 958.

[12] Prosen and Rossini, *J. Res. Nat. Bur. Stand.*, 1941, **27**, 289.

[13] Springall, White, and Cass, *Trans. Faraday Soc.*, 1954, **50**, 815.

independently by Drs. T. R. White and R. C. Cass.[3] The results were closely concordant. Data for one specimen are recorded (Table 3).

TABLE 2.

Wt. taken,* m (g.)	ΔR (ohm)	CO_2 (obs. : calc.)	Corrections (cal.) † (fuse)	Corrections (cal.) † (HNO_3)	C (cal./ohm)	$-\Delta U_b$ ‡ (kcal./mole)
5 : 5′-spiro*Bis*-1 : 3-*dioxan* (M, 160·17)						
0·6524	0·08998	0·9780	6·0	0·8	4·8	901·4
0·7116	0·09994	0·9978	6·0	0·8	5·3	899·8
0·8174	0·11475	0·9937	6·0	1·4	6·1	903·2
0·9154	0·12824	0·9969	6·0	3·5	6·8	898·2
0·9533	0·13379	0·9977	6·0	2·9	7·0	899·3
$E = 39980 \pm 10$ cal./ohm						
1 : 3-*Dioxan* (M, 88·10)						
0·4589	0·07448	0·9970	18·4	1·0	4·0	556·4
0·3720	0·05888	0·9747	20·0	0·7	3·2	553·7
0·4212	0·06858	0·9981	21·1	0·8	3·6	554·6
0·3831	0·06247	0·9975	10·4	0·8	3·3	554·6
$E = 39058 \pm 10$ cal./ohm						
1 : 3-*Dioxolan* (M, 74·05)						
0·4724	0·06664	0·9995	14·8	0·6	3·7	405·6
0·4781	0·06813	0·9994	22·5	1·3	3·7	408·3
0·6238	0·08836	0·9995	23·2	2·1	4·8	406·5
0·3923	0·05366	0·9997	28·6	1·3	3·0	404·8
$E = 39058 \pm 10$ cal./ohm						

* Weight *in vacuo.*

† Made necessary by heat effects due to the combustion of the fuse and the oxidation of nitrogen.

‡ Where $-\Delta U_b = 10^{-3}M/m'[(E + C)\Delta R - \text{Corr. (fuse} + HNO_3)]$ kcal./mole and $m' = m_{(vac.)} \times$ CO_2 (obs. : calc.).

TABLE 3.

Wt. taken,* m (g.)	$\Delta\theta$ (°)	θ_m (°)	Corrections (cal.).† (fuse)	Corrections (cal.).† (HNO_3)	Corrections (cal.).† (carbon)	E' (cal./deg.)	C (cal./deg.)	$-\Delta U_b$ ‡ (kcal./mole)
Paraldehyde (M, 132·16)								
1·2094	2·3453	4·210	71·8	3·8	2·3	3187·0	1·0	809·0
1·1663	2·2616	4·403	71·8	4·2	0·8	3192·0	1·0	809·8
1·1834	2·2944	4·406	71·8	3·8	0·8	3192·0	1·0	809·8

* Weight *in vacuo.*

† Made necessary by heat effects due to the combustion of the fuse, the oxidation of nitrogen, and deposition of some free carbon.

‡ Where $-\Delta U_b = 10^{-3}M/m[(E' + C)\Delta\theta - \text{corr. (fuse} + HNO_3 - \text{carbon)}]$ kcal./mole.

The $-\Delta U_b$ terms were converted into $-\Delta H_c°$ terms, the standard heat of combustion, by using the expression

$$-\Delta H_c° = -\Delta U_b - w - \Delta n\boldsymbol{R}T$$

where w is the Washburn correction, calculated according to Prosen,[14] and Δn is the number of moles of gas produced in the combustion reaction. The results are recorded in Table 4.

TABLE 4.

Compound	$-\Delta U_b$ mean (kcal./mole)	Standard deviation ($-\Delta U_b$) (%)	Overall uncertainty interval (%)	Washburn corr. w (kcal./mole)	$\Delta n\boldsymbol{R}T$ (kcal./mole)	$-\Delta H_c°$ (kcal./mole)
5 : 5′-*spiro*Bis-1 : 3-dioxan	900·4	±0·10	±0·14	0·6	−0·6	900·4
1 : 3-Dioxan	554·8	±0·23	±0·25	0·4	−0·6	555·0 *
1 : 3-Dioxolan	406·3	±0·20	±0·22	0·2	−0·3	406·4 *
Paraldehyde	809·5	±0·033	±0·042	0·4	−0·9	810·0

* Skuratov [15] has recently recorded slightly higher values of $-\Delta H_c°$ for these compounds (557·4 and 407·6 kcal./mole, respectively).

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[14] Prosen, " Experimental Thermochemistry," ed. Rossini, Interscience, New York, 1956.

[15] Skuratov, Kozina, Shteher, and Varushyenko, " IUPAC Thermochemical Bulletin," 1957, **3**.

DISCUSSION

The $-\Delta H_f^\circ$ terms for the compounds were calculated from $-\Delta H_c^\circ$ terms by using the values ΔH_f° for water = −68·32 and ΔH_f° for carbon dioxide = −94·05 kcal./mole.[16] By incorporating the L_v terms, the heats of atomisation, ΔH_a, C, 171·1,[17] H, 52·09,[16] and O, 58·98 kcal./g.-atom,[18] and atomic heats of formation, $-\Delta H_{f,g}^{a}$, were derived. From the values [2] $\bar{E}$(C–C) 83·1, $\bar{E}$(C–H) 98·85, and $\bar{E}$(C–O) 84·3 kcal./mole a summation was made of mean bond-energy terms in the molecule, $\sum\bar{E}$(b), and the difference, $-\Delta H_{f,g}^{a} - \sum\bar{E}$(b) = E_s, the stabilisation energy, was evaluated. Similar evaluations of E_s terms have been made from published $-\Delta H_c^\circ$ data for 4-methyl-1 : 3-dioxan (709·8;[15] assuming $L_v = 9$), *sym*-trioxan (356·7;[4] L_v = 9·6 [4]), 1 : 4-dioxan (554·6;[19] L_v = 8·5 [9]), and 1 : 2-diethoxyethane (924·6;[6] assuming $L_v = 10$) [all data in kcal./mole]. These data are given in Table 5.

TABLE 5.

Compound	Enthalpy terms		E_s (kcal./mole)
	$-\Delta H_{f,g}^{a}$	$\sum\bar{E}$(b)	
1 : 3-Dioxan	1307·4	1294·2	13·2
4-Methyl-1 : 3-dioxan	1600·4	1585·0	15·4
5 : 5′-*spiro*Bis-1 : 3-dioxan	2213·3	2193·0	20·3
sym-1 : 3 : 5-Trioxan	870·8	846·0	24·8
Paraldehyde	1731·8	1688·4	43·4
1 : 4-Dioxan	1307·2	1294·2	13·0
1 : 2-Diethoxyethane	1984·4	1970·4	14·0
1 : 3-Dioxolan	1017·8	1013·4	4·4

1 : 3-Dioxan has E_s = 13·2 kcal./mole. It is likely that the molecule is free from strain due to distortion of bond angles, as is that of 1 : 4-dioxan.[20] For 4-methyl-1 : 3-dioxan, the E_s term, 15·4 kcal./mole, is 2·2 kcal./mole greater than for 1 : 3-dioxan. This difference is similar to that between similar terms for *cyclo*hexane and methyl*cyclo*hexane, 2·6 kcal./mole,[21] so that the stabilisation energy due to the 1 : 3-dioxa-group in both compounds is 13 kcal./mole. With 5 : 5′-*spiro*bis-1 : 3-dioxan the E_s value, 20·3 kcal./mole, is somewhat less than twice this value.

This type of stabilisation has already been reported [3] in six-membered cyclic 1 : 3 : 5-trioxa-compounds, *sym*-trioxan (24·8 kcal./mole) and paraldehyde (43·4 kcal./mole). A similar, rather smaller effect is found in open-chain 1 : 3-dioxa-compounds, *i.e.*, the acetals, formaldehyde dimethyl acetal, formaldehyde diethyl acetal, and acetaldehyde dimethyl acetal which all show stabilisation energies of 7 kcal./mole.[6]

This additional stability is also found in molecules containing two oxygen atoms in the 1 : 4-position (*e.g.*, 1 : 4-dioxan, E_s = 13 kcal./mole; 1 : 2-diethoxyethane, E_s = 14 kcal./mole).

The stabilisation energy, E_s, of 1 : 3-dioxolan is 4·4 kcal./mole, whereas *cyclo*pentane has a " strain " energy of 6 kcal./mole (E_s = −6 kcal./mole).[22] It is probable that the molecules of both these compounds are free from strain due to distortion of bond angles, the strain observed in *cyclo*pentane being due mainly to repulsive forces between hydrogen atoms bonded to adjacent carbon atoms.[23] [With tetrahydrofuran the strain is reduced [2] to 3 kcal./mole (E_s = −3 kcal./mole).]

These C–O bonds have [20] the length (1·42 ± 0·03 Å) of normal C–O single bonds.[24] It seems likely that the cause of the stabilisation of the di- and tri-oxa-compounds, relative to the corresponding saturated hydrocarbons, is reduction in the repulsive forces between non-bonded hydrogen atoms, arising from the replacement of the $\cdot CH_2\cdot CH_2\cdot CH_2\cdot$ systems

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[16] National Bureau of Standards Circular 500, Washington, 1952.

[17] Brewer and Kane, *J. Phys. Chem.*, 1955, **59**, 105.

[18] Brix and Herzberg, *J. Chem. Phys.*, 1953, **22**, 2240.

[19] Roth and Meyer, *Z. Elektrochem.*, 1933, **39**, 35.

[20] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.

[21] Selected Values of Properties of Hydrocarbons, American Petroleum Institute, Research Project 44, 1954.

[22] Dolliver, Gresham, Kistiakowsky, and Vaughan, *J. Amer. Chem. Soc.*, 1937, **59**, 831.

[23] Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N.Y., 1940, p. 91.

[24] *Idem, op. cit.*, p. 167.

by $\cdot CH_2\cdot O\cdot CH_2$ systems. Even so the high degree of stabilisation shown by paraldehyde and the low degree shown by the open-chain acetals seem anomalous.

It is probably not legitimate to press the analysis further because, as Sidgwick [25] and others (*e.g.*, Dewar [26]) have pointed out, for a rigorous intramolecular structural analysis, enthalpy terms should be measured at, or corrected to, 0° K (ΔH_0 terms). For a given change in a particular molecular system, the thermochemically measured $\Delta H'_{298}$ term is related to the corresponding $\Delta H'_0$ term by the Kirchhoff expression

$$\Delta H'_{298} = \Delta H'_0 + \int_0^{298} \Delta C'_p \mathrm{d}T,$$

where $\Delta C'_p$ is the change in the specific heat of the system during the reaction at a particular temperature. The $\Delta C'_p$ integral term, which accounts for the kinetic component of $\Delta H'_{298}$ not included in the zero-point energy, is usually unknown but is normally small relative to $\Delta H'_0$.

When considering the difference between this $\Delta H'_{298}$ and the $\Delta H''_{298}$ for the corresponding change in another system (the standard procedure in thermochemical studies on molecular structure), we have

$$\Delta H'_{298} - \Delta H''_{298} = \Delta H'_0 - \Delta H''_0 + \int_0^{298} (\Delta C'_p - \Delta C''_p)\mathrm{d}T$$

Provided $\Delta H'_{298} - \Delta H''_{298}$ is large it may reasonably be taken as a measure of $\Delta H'_0 - \Delta H''_0$ and we may neglect the heat component due to the ΔC_p integrals. When, however, $\Delta H'_{298} - \Delta H''_{298}$ is small, it cannot safely be taken as a measure of $\Delta H'_0 - \Delta H''_0$ because the term due to the ΔC_p integrals may be of comparable magnitude. As Dewar [26] has pointed out, there is no reason why this integral term should be susceptible to analysis into constant bond components, and there are grounds for expecting that in formation reactions it will be larger for an open-chain compound than for a ring analogue.

We are indebted to Imperial Chemical Industries Limited for a grant.

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[25] Sidgwick, " The Covalent Link in Chemistry," Cornell Univ. Press, Ithaca, N.Y., 1933, p. 101.
[26] Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767.