525. *Heats of Combustion and Molecular Structure. Part VI.* The Structure of Some Cyclic Ethers of* o-*Dihydroxybenzene.*

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The heats of combustion of *o*-dimethoxybenzene, 1 : 3-dioxaindane, 1 : 4-dioxatetralin, and 2 : 3-benzo-1 : 4-dioxa*cyclo*heptane have been measured. The resonance energies are derived and are discussed in terms of the structures of the non-aromatic groupings.

Experimental

Materials.—*o*-Dimethoxybenzene (from Messrs. Hopkin and Williams) was distilled through a 6″ Fenske column. The fraction collected had b. p. 205·5°/748 mm. Heilbron and Bunbury [1] give b. p. 206°/759 mm.

1 : 3-Dioxaindane (1 : 3-benzodioxole) was prepared by the method suggested by Baker,[2] from methylene sulphate and *o*-dihydroxybenzene. Distilled through an 18″ Fenske column, the fraction collected had b. p. 173·2—173·5°/758 mm. Baker [2] gives b. p. 173—174°/756 mm.

1 : 4-Dioxatetralin (2 : 3-dihydrobenzo-1 : 4-dioxan) was prepared from ethylene bromide and *o*-dihydroxybenzene in the presence of potassium carbonate, copper bronze, and glycerol.[3] It distilled at 213·2°/774 mm. Gattermann [3] gives b. p. 206—207°/749 mm.

2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene (6 : 7-dihydro-2 : 3-benzo-1 : 4-dioxepin) was prepared by heating *o*-dihydroxybenzene (27·5 g.), 1 : 3-dibromopropane (50 g.), finely powdered anhydrous potassium carbonate (35 g.), glycerol (1 g.), and copper bronze (1 g.) under reflux for 10 hr.[4] The mixture was cooled, diluted with water (30 ml.), and made faintly alkaline with sodium hydroxide, then steam-distilled, and the distillate was extracted with chloroform. The chloroform layer was separated, dried (Na_2SO_4), and distilled. The product was distilled through a 6″ Fenske column, the fraction collected having b. p. 100·5°/11 mm (Found: C, 72·0; H, 6·6. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%).

Vapour-pressure Measurement.—The vapour pressures of the compounds were measured in an apparatus of the type described by Sanderson.[5] The values of A and B of the equation $\log_{10} p_{mm.} = -A/T + B$ 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.

Table 1.

Compound	A	B	L_v (kcal./mole)
o-Dimethoxybenzene	3492·0	9·58	16·0
1 : 3-Dioxaindane	2164·1	7·69	9·90
1 : 4-Dioxatetralin	2633·7	8·27	12·05
2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene	2918·3	8·8	13·28

Combustion Calorimetry.—*o*-Dimethoxybenzene was burnt in a twin-valve bomb (The Parr Instrument Company, Moline, Illinois, U.S.A.) of energy equivalent, $E = 39{,}058 \pm 20$ cal./ohm, the temperature changes being recorded by a platinum resistance thermometer. Details of the experimental procedure and method of calculation have been given in Parts III and IV of this series. The amount of carbon dioxide present in the bomb gases after combustion was determined; the theoretical quantity was deficient by an amount which corresponded closely to the weight of carbon remaining in the bomb after combustion. A correction was made by taking the heat of combustion of amorphous carbon as 8·11 kcal./g. Combustions of the remaining compounds were made in a stainless-steel, single-valve, Mahler–Cook bomb of energy equivalent, $E = 31{,}199 \pm 8{\cdot}0$ cal./ohm, according to the procedure described in Part III. The results are shown in Table 2.

* Parts I—V, *Trans. Faraday Soc.*, 1954, **50**, 815; *J.*, 1954, 2764; 1955, 1188; 1958, 958, 1406.

[1] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1953.
[2] Baker, *J.*, 1931, 1765.
[3] Gattermann, *Annalen*, 1907, **375**, 373.
[4] Ghosh, *J.*, 1915, **107**, 1591.
[5] Sanderson, " Vacuum Manipulation of Volatile Compounds," Wiley, New York, 1948, p. 48.

TABLE 2.

Weight taken * (m) (g.)	ΔR (ohms)	Corrections (cal.) Fuse	HNO_3	Carbon	C (cal./ohm)	$-\Delta U_b$ (kcal./mole)
		o-Dimethoxybenzene, M 138·16				
0·6606	0·12555	14·3	2·4	8·9	4·8	1023·9
0·3951	0·07509	17·9	1·3	13·9	2·4	1023·5
0·5701	0·10851	16·3	2·0	7·7	4·1	1024·5
0·3648	0·06902	14·8	1·3	3·9	2·6	1025·2
		1 : 3-*Dioxaindane, M* 122·12				
0·9977	0·21553	113·7	0·1	0·3	7·0	820·5
0·9726	0·20910	89·9	0·2	0·8	7·0	819·5
1·0014	0·21491	80·1	0·7	0·8	7·0	819·1
		1 : 4-*Dioxatetralin, M* 136·14				
1·0356	0·23776	84·7	3·4	0·7	8·0	964·8
0·69305	0·15933	59·5	0·2	3·9	4·0	965·1
0·66713	0·15346	67·4	0·2	3·5	4·0	964·4
		2 : 3-*Benzo*-1 : 4-*dioxa*cyclo*heptene, M* 150·17				
0·9454	0·23102	87·8	1·4	—	6·0	1130·4
0·8915	0·21032	83·4	2·1	2·9	6·0	1130·2
0·8244	0·20193	93·0	2·5	0·3	6·0	1130·1

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

* Weight *in vacuo*.

The $-\Delta U_b$ terms were converted into $-\Delta H_c^\circ$ terms, the standard heat of combustion (Table 3), by using the expression

$$-\Delta H_c^\circ = -\Delta U_b - w - \Delta n\boldsymbol{R}T,$$

where w is the Washburn correction, calculated by Prosen's method,[6] and Δn is the number of moles of gas produced in the combustion.

TABLE 3.

Compound	$-\Delta U_b$ mean (kcal./mole)	Standard deviation ($-\Delta U_b$) (%)	Overall standard deviation (%)	Washburn corr. w (kcal./mole)	$\Delta n\boldsymbol{R}T$ (kcal./mole)	$-\Delta H_c^\circ$ (kcal./mole)
o-Dimethoxybenzene	1024·2	0·047	0·050	0·6	−0·3	1023·9 ± 0·5
1 : 3-Dioxaindane ...	819·6	0·061	0·072	0·6	−0·3	819·3 ± 0·5
1 : 4-Dioxatetralin ...	964·8	0·028	0·035	0·7	−0·6	964·7 ± 0·3
2 : 3-Benzo-1 : 4-dioxa-*cyclo*heptene	1130·2	0·018	0·020	0·8	−0·9	1130·3 ± 0·2

DISCUSSION

The $-\Delta H_{f,g}^{st}$ terms for the compounds were calculated from $-\Delta H_c^\circ$ and L_v terms by using $\Delta H_f^\circ H_2O(l.) = -68{\cdot}32$ and $\Delta H_f^\circ CO_2(g.) = -94{\cdot}05$ kcal./mole. By incorporating the ΔH_a terms, C, 171·7;[7] H, 52·09;[8] O, 58·98 kcal./g.-atom,[9] the $-\Delta H_{f,g}^a$ terms were derived. A summation was made of the mean bond-energy terms in the molecule, $\Sigma\bar{E}(b)$, the values $\bar{E}$(C–C), 83·1; $\bar{E}$(CH=CH, *cis*), 148·2; $\bar{E}$(C–H), 98·85 (Part II); and $\bar{E}$(C–O), 84·3 kcal./mole, being used (Part V). The difference, $-\Delta H_{f,g}^a\ \Sigma\bar{E}(b) = E_r$, was evaluated. These values are given in Table 4.

The variation in the resonance energy is correlated with the difference in structure of the non-aromatic rings.

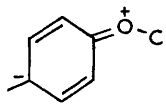
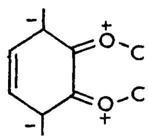
It has been shown in Part V that the resonance energy of the C_6H_5O system is of the order of 42 kcal./mole, due to contributions from ionic forms of the type (I). (The resonance energy of the C_6H_5C system is 38·9 kcal./mole.)

[6] Prosen, " Experimental Thermochemistry," ed. Rossini, Interscience, New York, 1956.
[7] Brewer and Kane, *J. Phys. Chem.*, 1955, **59**, 105.
[8] Nat. Bur. Stand., Circular 500, Washington, 1952.
[9] Brix and Herzberg, *J. Chem. Phys.*, 1953, **21**, 2240.

TABLE 4.

Compound	$-\Delta H_{f,g}{}^{a}$	$\Sigma\bar{E}(b)$ (kcal./mole)	E_r (kcal./mole)
o-Dimethoxybenzene	2066·6	2019·6	47·0
1 : 3-Dioxaindane	1664·2	1625·8	38·4
1 : 4-Dioxatetralin	1954·4	1906·6	47·8
2 : 3-Benzo-1 : 4-dioxa*cyclo*heptene	2225·5	2187·4	38·1

It is to be expected that the resonance energy of the *o*-$C_6H_4O_2$ system will exceed that of the C_6H_5O system, owing to the increased number of ionic forms [including those of the type (II)].

(I)   (II)

The resonance energies for *o*-dimethoxybenzene and 1 : 4-dioxatetralin are some 5 kcal./mole greater than for the C_6H_5O system, while those for 1 : 3-dioxaindane and 2 : 3-benzo-1 : 4-dioxa*cyclo*heptene are about 4 kcal./mole less. Resonance of types (I) and (II) is favoured if (i) the $C_{ar.}$–O–$C_{al.}$ angle can be 121° ± 2°,[10] and (ii) if the O–$C_{al.}$ fragment of the side-chain can be coplanar with the aromatic nucleus. A simple consideration of scale models, with 110° for the unstrained $-CH_2-$ angle, and the normal interatomic distances $C_{ar.}$–O, 1·36 Å;[10] $C_{al.}$–O, 1·42 Å; and $C_{al.}$–$C_{al.}$, 1·54 Å [11] shows that the conditions (i) and (ii) can be satisfied with *o*-dimethoxybenzene and with 1 : 4-dioxatetralin, but not with 1 : 3-dioxaindane, in which, though the whole molecule is planar, the $C_{ar.}$–O–$C_{al.}$ angle must be much less than 125°, or with 2 : 3-benzo-1 : 4-dioxa*cyclo*heptene. These steric considerations are thus compatible with the experimental findings and with those from dipole-moment studies.[12]

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[10] Goodwin, Przyblska, and Robertson, *Acta Cryst.*, 1950, **3**, 279.
[11] Allen and Sutton, *Acta Cryst.*, 1950, **3**, 46.
[12] Springall, Hampson, May, and Spedding, *J.*, 1949, 1524.