708. *Physical Properties and Chemical Constitution. Part XXVII.* Dipole Moments of Some Cyclic Ethers, Sulphides, Sulphoxides, and Sulphones.*

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The orientation polarisations and dipole moments of four cyclic organic sulphides, and the related sulphoxides and sulphones, have been calculated from measurements of the dielectric constants, specific volumes, and refractive indices of their solutions in benzene. The dipole moments are discussed in terms of the moment of the sulphur–oxygen link and the geometrical structure of the molecules. The dipole moments of five cyclic ethers have also been measured, and the carbon–oxygen bond moment evaluated and compared with that of non-cyclic ethers.

THE electric dipole moments of several organic sulphides, sulphoxides, and sulphones are recorded in the literature but only in four cases have the moments of the sulphide and the corresponding sulphoxide and sulphone been measured. No cyclic sulphoxides or sulphones have been investigated.

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* Part XXVI, 1957, 3640.

The dipole moments of several cyclic organic sulphides and the related sulphoxides and sulphones, determined in benzene solution, are now reported and are discussed in terms of the moment of the sulphur–oxygen bond and the geometrical structure of the molecules. The dipole moments of some cyclic ethers are also considered.

EXPERIMENTAL

The apparatus and techniques used were described in Part XXV.[1] Observations were made in benzene solution at 25·00° ± 0·01°. The sulphoxides are hygroscopic and were handled in a dry box. Solutions of the more volatile ethers were prepared by adding the ether to the benzene in Pyrex glass-stoppered bottles so as to reduce loss by evaporation.

Thiacyclopentane oxide and dioxide, 1,4-thioxan, propene oxide, tetrahydrofuran, tetrahydropyran, and 1,3-dioxolan were high-grade commercial products; trimethylene oxide was prepared by Mr. D. G. Redford, B.Sc., and the other substances by Dr. R. S. Parker of this laboratory, who also extensively purified each compound. The sulphides, which were then used for the preparation of the sulphoxides and sulphones, and the ethers were tested for purity by gas-chromatography and shown to give one peak each (a Griffin & George Ltd. Mark IIA apparatus was used with silicone grease on Celite as the stationary phase). Details of the preparations, together with other physical properties, will be published later.

RESULTS

The dielectric constants (ε_{12}), specific volumes (v_{12}), and refractive indices to sodium light (n_{12}) of benzene solutions with weight fractions w_2 are recorded in Table 1. Over the concentration range studied, ε_{12} was a linear function of w_2, and the parameters of this relation, determined by a method of least squares, are also in Table 1. Likewise v_{12} and the specific refraction (r_{12}) of the solutions were linear functions of w_2.

The total polarisation of the solutes, when extrapolated to infinite dilution, ($_{\infty}P_2$) was evaluated (see Table 2). The distortion polarisation, to be subtracted from $_{\infty}P_2$ to give the orientation polarisation ($_{\text{O}}P$), was assumed equal to the molar refraction to sodium light (R_{D}) and obtained from the specific refraction of the solutions.[1] The values of R_{D}, $_{\text{O}}P$ and the electric dipole moment (μ) of the compounds [calculated from the usual formula, $\mu = 0{\cdot}01281\sqrt{(_{\text{O}}PT)}$] are also given in Table 2. A large atom polarisation could result in a significant error in the dipole moment of 1,4-thioxan.

DISCUSSION

(a) *Sulphides, Sulphoxides, and Sulphones.*—In a previous paper[2] the dipole moment change ($\Delta\mu_{\text{SO}}$) in the direction of the S–O bond, when a sulphide is converted into the sulphoxide or sulphone, was discussed. It was assumed that the CSC angle in the sulphides was unchanged on oxidation and that the oxygen atom(s) were always inclined at the same angle (θ) to the CSC plane. If θ was assigned the reasonable value of 61·5°, $\Delta\mu_{\text{SO}}$ was found to be 3·0 D in aliphatic sulphoxides and sulphones. This value is also in agreement with the dipole moments of several sulphones measured by Lumbroso and Passerini.[3]

A somewhat larger value for $\Delta\mu_{\text{SO}}$ is found if the sulphur atom is attached to a benzene ring—probably caused by larger induced moments and a change in the conjugation between them (the S–O bond is thought not to enter into conjugation [4]).

The results for the present compounds may be interpreted in two ways depending on the assumptions made.

(*a*) By applying vector analysis, as in the non-cyclic compounds considered previously,[2]

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[1] Cumper, Vogel, and Walker, *J.*, 1956, 3621.

[2] Cumper and Walker, *Trans. Faraday Soc.*, 1956, **52**, 193.

[3] Lumbroso and Passerini, *Bull. Soc. chim. France*, 1955, 1179.

[4] Price and Morita, *J. Amer. Chem. Soc.*, 1953, **75**, 4747; Price and Gillis, *ibid.*, 1953, **75**, 4750; Baliah and Shanmuganathan, *Trans. Faraday Soc.*, 1959, **55**, 232.

TABLE 1.

Thiacyclobutane (1)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000826	1·14430	2·2765	1·49788
0·002084	1·14408	2·2822	1·49790
0·005499	1·14352	2·2982	1·49791
0·008783	1·14293	2·3133	1·49790
0·012150	1·14240	2·3290	1·49794
0·016094	1·14172	2·3472	1·49798
0·017023	1·14158	2·3518	1·49800

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}149w_2)$
$\epsilon_{12} = 2{\cdot}2726_3\ (1 + 2{\cdot}04_1w_2)$
$r_{12} = 0{\cdot}33538\ (1 - 0{\cdot}135_3w_2)$

Thiacyclobutane dioxide (2)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000618	1·14419	2·2852	1·49770
0·001536	1·14380	2·3039	1·49770
0·004339	1·14257	2·3621	1·49767
0·007241	1·14125	2·4223	1·49769
0·012549	1·13892	2·5308	1·49766
0·013079	1·13860	2·5437	1·49766
0·016303	1·13720	2·6083	1·49765

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}387w_2)$
$\epsilon_{12} = 2{\cdot}2724_4\ (1 + 9{\cdot}07_4w_2)$
$r_{12} = 0{\cdot}33531\ (1 - 0{\cdot}397_2w_2)$

Thiacyclopentane (3)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000974	1·14430	2·2769	1·49776
0·001932	1·14421	2·2810	1·49777
0·004211	1·14383	2·2916	1·49778
0·006054	1·14357	2·2997	1·49778
0·010840	1·14289	2·3206	1·49780
0·015707	1·14218	2·3423	1·49784
0·017342	1·14193	2·3501	1·49785

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}126w_2)$
$\epsilon_{12} = 2{\cdot}2726_4\ (1 + 1{\cdot}95_6w_2)$
$r_{12} = 0{\cdot}33532\ (1 - 0{\cdot}117_8w_2)$

Thiacyclopentane oxide (4)

w_2	v_{12}	ϵ_{12}	n_{12}
0·001563	1·14393	2·3008	1·49787
0·001633	1·14392	2·3022	1·49787
0·003154	1·14335	2·3293	1·49795
0·004937	1·14271	2·3624	1·49803
0·010235	1·14083	2·4593	1·49826
0·010306	1·14078	2·4608	1·49829
0·017860	1·13822	2·5978	1·49854

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}307w_2)$
$\epsilon_{12} = 2{\cdot}2723_4\ (1 + 8{\cdot}02_3w_2)$
$r_{12} = 0{\cdot}33536\ (1 - 0{\cdot}235_9w_2)$

Thiacyclopentane dioxide (5)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000769	1·14409	2·2883	1·49787
0·000869	1·14408	2·2910	1·49784
0·003805	1·14288	2·3522	1·49788
0·005347	1·14222	2·3845	1·49792
0·007686	1·14116	2·4338	1·49800
0·010625	1·13995	2·4948	1·49805
0·018329	1·13670	2·6561	1·49820

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}370w_2)$
$\epsilon_{12} = 2{\cdot}2726_1\ (1 + 9{\cdot}20_7w_2)$
$r_{12} = 0{\cdot}33539\ (1 - 0{\cdot}333_9w_2)$

Thiacyclohexane (6)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000833	1·14435	2·2752	1·49776
0·002873	1·14410	2·2814	1·49777
0·003608	1·14400	2·2842	1·49777
0·008129	1·14344	2·2979	1·49779
0·012479	1·14290	2·3115	1·49781
0·016671	1·14238	2·3245	1·49784
0·018117	1·14220	2·3297	1·49784

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}108w_2)$
$\epsilon_{12} = 2{\cdot}2726_5\ (1 + 1{\cdot}36_9w_2)$
$r_{12} = 0{\cdot}33532\ (1 - 0{\cdot}100_5w_2)$

Thiacyclohexane oxide (7)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000300	1·14436	2·2775	1·49787
0·000946	1·14418	2·2873	1·49790
0·002025	1·14376	2·3053	1·49789
0·003407	1·14344	2·3274	1·49799
0·007500	1·14211	2·3936	1·49811
0·010272	1·14123	2·4386	1·49823
0·018072	1·13878	2·5652	1·49854

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}273w_2)$
$\epsilon_{12} = 2{\cdot}2723_5\ (1 + 7{\cdot}13_4w_2)$
$r_{12} = 0{\cdot}33538\ (1 - 0{\cdot}200_3w_2)$

Thiacyclohexane dioxide (8)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000396	1·14430	2·2801	1·49773
0·001080	1·14404	2·2929	1·49774
0·002717	1·14342	2·3238	1·49778
0·004228	1·14285	2·3524	1·49780
0·005788	1·14216	2·3820	1·49787
0·009178	1·14092	2·4455	1·49791
0·011789	1·13985	2·4946	1·49799

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}338w_2)$
$\epsilon_{12} = 2{\cdot}2726_7\ (1 + 8{\cdot}28_8w_2)$
$r_{12} = 0{\cdot}33530\ (1 - 0{\cdot}298_8w_2)$

1,4-*Thioxan* (9)

w_2	v_{12}	ϵ_{12}	n_{12}
0·002442	1·14382	2·2731	1·49781
0·008950	1·14214	2·2744	1·49790
0·016443	1·14021	2·2757	1·49800
0·021181	1·13895	2·2767	1·49808
0·027888	1·13729	2·2780	1·49811
0·032492	1·13606	2·2789	1·49820
0·036327	1·13506	2·2797	1·49825

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}226w_2)$
$\epsilon_{12} = 2{\cdot}2725_7\ (1 + 0{\cdot}086_1w_2)$
$r_{12} = 0{\cdot}33534\ (1 - 0{\cdot}204_3w_2)$

1,4-*Thioxan oxide* (10)

w_2	v_{12}	ϵ_{12}	n_{12}
0·001937	1·14357	2·2879	1·49783
0·002788	1·14321	2·2943	1·49791
0·007551	1·14127	2·3314	1·49808
0·009052	1·14051	2·3436	1·49816
0·012377	1·13910	2·3693	1·49826
0·016411	1·13742	2·4007	1·49841
0·018652	1·13645	2·4187	1·49851

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}376w_2)$
$\epsilon_{12} = 2{\cdot}2725_8\ (1 + 3{\cdot}44_2w_2)$
$r_{12} = 0{\cdot}33533\ (1 - 0{\cdot}309_8w_2)$

1,4-*Thioxan dioxide* (11)

w_2	v_{12}	ϵ_{12}	n_{12}
0·001203	1·14390	2·2828	1·49784
0·002228	1·14339	2·2917	1·49784
0·004603	1·14231	2·3120	1·49786
0·004827	1·14222	2·3141	1·49786
0·005047	1·14209	2·3162	1·49786
0·009678	1·13998	2·3561	1·49790
0·014300	1·13788	2·3959	1·49794

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}404w_2)$
$\epsilon_{12} = 2{\cdot}2725_0\ (1 + 3{\cdot}79_9w_2)$
$r_{12} = 0{\cdot}33536\ (1 - 0{\cdot}386_9w_2)$

Propylene oxide (12)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000531	1·14450	2·2761	1·49772
0·001075	1·14452	2·2800	1·49768
0·004845	1·14475	2·3050	1·49718
0·009235	1·14506	2·3344	1·49657
0·014399	1·14541	2·3689	1·49590
0·015948	1·14552	2·3794	1·49574
0·017908	1·14566	2·3924	1·49543

$v_{12} = 1{\cdot}14445\ (1 + 0{\cdot}067w_2)$
$\epsilon_{12} = 2{\cdot}2726_3\ (1 + 2{\cdot}94_3w_2)$
$r_{12} = 0{\cdot}33535\ (1 - 0{\cdot}168_0w_2)$

Trimethylene oxide (13)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000682	1·14444	2·2768	1·49780
0·001457	1·14442	2·2819	1·49768
0·003741	1·14432	2·2973	1·49748
0·006317	1·14425	2·3143	1·49718
0·010801	1·14411	2·3435	1·49679
0·013239	1·14403	2·3599	1·49653
0·017177	1·14393	2·3855	1·49612

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}027w_2)$
$\epsilon_{12} = 2{\cdot}2725_1\ (1 + 2{\cdot}89_8w_2)$
$r_{12} = 0{\cdot}33537\ (1 - 0{\cdot}196_6w_2)$

Tetrahydrofuran (14)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000518	1·14445	2·2748	1·49776
0·001522	1·14444	2·2791	1·49769
0·004838	1·14438	2·2932	1·49743
0·005913	1·14434	2·2981	1·49728
0·009679	1·14425	2·3143	1·49692
0·013708	1·14419	2·3315	1·49661
0·014608	1·14415	2·3355	1·49650

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}017w_2)$
$\epsilon_{12} = 2{\cdot}2725_4\ (1 + 1{\cdot}89_4w_2)$
$r_{12} = 0{\cdot}33536\ (1 - 0{\cdot}173_1w_2)$

Tetrahydropyran (15)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000917	1·14445	2·2750	1·49783
0·001699	1·14444	2·2773	1·49774
0·004527	1·14441	2·2852	1·49753
0·006418	1·14439	2·2905	1·49741
0·009354	1·14435	2·2987	1·49717
0·014397	1·14429	2·3128	1·49674
0·017689	1·14426	2·3218	1·49652

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}010w_2)$
$\epsilon_{12} = 2{\cdot}2725_7\ (1 + 1{\cdot}22_6w_2)$
$r_{12} = 0{\cdot}33539\ (1 - 0{\cdot}139_2w_2)$

1,3-*Dioxolan* (16)

w_2	v_{12}	ϵ_{12}	n_{12}
0·000942	1·14426	2·2754	1·49774
0·002122	1·14402	2·2786	1·49765
0·004601	1·14351	2·2863	1·49749
0·007754	1·14285	2·2951	1·49720
0·013463	1·14169	2·3117	1·49678
0·017560	1·14083	2·3236	1·49648
0·018262	1·14072	2·3259	1·49646

$v_{12} = 1{\cdot}14445\ (1 - 0{\cdot}179w_2)$
$\epsilon_{12} = 2{\cdot}2726_0\ (1 + 1{\cdot}28_1w_2)$
$r_{12} = 0{\cdot}33536\ (1 - 0{\cdot}309_8w_2)$

TABLE 2.

Compound		$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	$_0P$ (cm.^{3})	μ_D	Previous vals. for C_6H_6 soln.
C_3H_6S	(1)	86·21	21·51	64·70	1·78	
$C_3H_6SO_2$	(2)	433·9	21·47	412·4	4·49	
C_4H_8S	(3)	99·98	26·09	73·89	1·90	1·87[a]
C_4H_8SO	(4)	381·8	26·70	355·1	4·17	
$C_4H_8SO_2$	(5)	498·7	26·85	471·8	4·81	
$C_5H_{10}S$	(6)	90·86	30·83	60·03	1·71	
$C_5H_{10}SO$	(7)	389·7	31·71	358·0	4·19	
$C_5H_{10}SO_2$	(8)	505·7	31·56	474·1	4·82	
OC_4H_8S	(9)	31·33	27·80	3·53	0·42	0·47[b]
OC_4H_8SO	(10)	202·3	27·82	174·5	2·92	
$OC_4H_8SO_2$	(11)	248·8	28·01	220·8	3·29	
$CH_3C_2H_3O$	(12)	94·02	16·21	77·81	1·95	1·88[c], 1·98[d]
C_3H_6O	(13)	91·20	15·65	75·55	1·92	2·01[c]
C_4H_8O	(14)	82·55	20·00	62·55	1·75	1·68[a], 1·71[e]
$C_5H_{10}O$	(15)	74·22	24·87	49·35	1·55	1·87[c]
$C_3H_6O_2$	(16)	61·28	17·15	44·13	1·47	
RR′S *					1·59	
$RR'SO_2$ *					4·46	

* Average values [2] for R, R′ = Et, Pr^n, Bu^n, *n*-C_5H_{11}.

[a] Robles, *Rec. Trav. chim.*, 1939, **58**, 111. [b] Henriques, *ibid.*, 1934, **53**, 1139; Boeseken, Tellegen, and Henriques, *ibid.*, 1935, **54**, 733. [c] Allen and Hibbert, *J. Amer. Chem. Soc.*, 1934, **56**, 1398. [d] Rogers, *ibid.*, 1947, **69**, 2544. [e] Smyth and Walls, *ibid.*, 1932, **54**, 3230.

the results in Table 3 are obtained. Column 2 gives the values evaluated for $\Delta\mu_{SO}$ if the angle θ is assumed to be 61·5°; column 3 gives the angle θ required to account for the experimental dipole moments if $\Delta\mu_{SO}$ is taken as 3·00 D. In this analysis an additional assumption is made, that the resultant moment of the sulphide acts in the CSC plane.

TABLE 3.

Compound		$\Delta\mu_{SO}$ (θ = 61·5°)	θ ($\Delta\mu_{SO}$ = 3·00 D)	Compound		$\Delta\mu_{SO}$ (θ = 61·5°)	θ ($\Delta\mu_{SO}$ = 3·00 D)
$C_3H_6SO_2$	(2)	2·84 D	63·1°	$C_5H_{10}SO_2$	(8)	3·25	58·8°
C_4H_8SO	(4)	2·91	65·3	OC_4H_8SO	(10)	2·70	104·1
$C_4H_8SO_2$	(5)	3·04	61·0	$OC_4H_8SO_2$	(11)	3·01	61·4
$C_5H_{10}SO$	(7)	3·09	57·1	$RR'SO_2$		3·01	61·4

(*b*) Thiacyclobutane almost certainly has a planar ring [5] but it has been reported that this is not the case for cyclopentane [6] and it would be less likely for thiacyclopentane.[7] Thiacyclohexane [8] and 1,4-thioxan have distorted chair conformations. Consequently, since the C–H bond is polar [9] the resultant moments of thiacyclopentane, thiacyclohexane, and 1,4-thioxan cannot lie in the CSC plane.

The dipole moments of the cyclic sulphides, sulphoxides, and sulphones may be expressed by the following equations, in which X is the resultant (opposing) dipole moment of the C–H bonds (together with the C–O bonds in 1,4-thioxan) and the induced moments in the C–C bonds, and ϕ the angle between the direction of X and the resultant moment of the two C–S bonds (μ_{CS}).

Sulphide

$$\mu^2 = \left[2\mu_{CS}\cos\frac{\angle CSC}{2} + X\cos\phi\right]^2 + [X\sin\phi]^2$$

Sulphoxide

$$\mu^2 = \left[2\mu_{CS}\cos\frac{\angle CSC}{2} + X\cos\phi + \Delta\mu_{SO}\cos\theta\right]^2 + [X\sin\phi \pm \Delta\mu_{SO}\sin\theta]^2$$

Sulphone

$$\mu^2 = \left[2\mu_{CS}\cos\frac{\angle CSC}{2} + X\cos\phi + 2\Delta\mu_{SO}\cos\theta\right]^2 + [X\sin\phi]^2$$

The angle θ can be evaluated from the above equations if one assumes that the angle CSC is constant and that $\Delta\mu_{SO}$ is 3·00 D in both sulphoxides and sulphones; the results are presented in Table 4. The CSO angle is remarkably constant in many sulphoxides and sulphones [10] at about 107°, and if this value is assumed for these cyclic molecules the CSC angle may be calculated from the relation:

$$-\cos\angle CSO = \cos\tfrac{1}{2}\angle OSO \cos\tfrac{1}{2}\angle CSC$$

In each case the results seem plausible and the relative values consistent. Since $\Delta\mu_{SO}$ and θ are not independent of one another, the angles θ for the cyclic compounds will depend on the value of θ assumed for the alkyl sulphoxides and sulphones. It is also possible that $\Delta\mu_{SO}$ may differ slightly between a sulphoxide and the corresponding sulphone; but the experimental data are at present insufficient to decide this point. Further, if the $\overset{+\!\!\longrightarrow}{\text{C—S}}$

[5] Scott, Finke, Hubbard, McCullough, Katz, Gross, Messerly, Pennington, and Waddington, *J. Amer. Chem. Soc.*, 1953, **75**, 2795.

[6] Kilpatrick, Pitzer, and Spitzer, *ibid.*, 1947, **69**, 2483; Miller and Inskeep, *J. Chem. Phys.*, 1950, **18**, 1510; Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1956, 54.

[7] Hubbard, Finke, Scott, McCullough, Katz, Gross, Messerly, Pennington, and Waddington, *J. Amer. Chem. Soc.*, 1952, **74**, 6025.

[8] McCullough, Finke, Hubbard, Good, Pennington, Messerly, and Waddington, *ibid.*, 1954, **76**, 2661.

[9] Smith, " Electric Dipole Moments," Butterworths, London, 1955, p. 125.

[10] Abrahams, *Quart. Rev.*, 1956, **10**, 407.

bond moment μ_{CS} is known, X and ϕ can also be evaluated, though they have little significance. The values quoted in Table 4 are evaluated on the assumption that $\mu_{CS} = 1{\cdot}60$ D.†

In thiacyclobutane the CSC angle would be between the bonding orbitals of the sulphur atom rather than the actual bond angle. The above analysis shows that the S–O and X moments are *trans* to one another in the thiacyclopentane and 1,4-thioxan oxides, but *cis* in thiacyclohexane oxide. The oxide oxygen atom is probably in the equatorial position in each case.

TABLE 4.

Compounds	θ	∠CSC	ϕ	X (D)
C_3H_6S (1), $C_3H_6SO_2$ (2)	63·1°	99·4°	0·0°	−0·29
C_4H_8S (3), C_4H_8SO (4), $C_4H_8SO_2$ (5)	61·0	105·8	72·5	−0·15
$C_5H_{10}S$ (6), $C_5H_{10}SO$ (7), $C_5H_{10}SO_2$ (8)	58·9	111·0	27·6	−0·11
OC_4H_8S (9), OC_4H_8SO (10), $OC_4H_8SO_2$ (11)	60·3	107·8	10·4	−1·61
RR′S, RR′SO_2	61·4	104·5	0·0	−0·37

(b) *Ethers.*—The dipole moments of some cyclic ethers were measured for comparison with the cyclic sulphides. Since the C–O bond is shorter than a C–S bond, ring systems containing oxygen would be expected to be less distorted than the corresponding sulphides.

The apparent C–O bond moments, without allowance for induced moments, calculated for various COC bond angles are given in Table 5 ($\mu_{\overset{+\rightarrow}{\mathrm{C-H}}} = 0{\cdot}30$ D).

The boiling point of ethylene oxide is somewhat low for this compound to be studied adequately in solution (its dipole moment has been reported[11] as 1·88 and 1·85 D), but should be slightly less than that of propylene oxide because of the moment induced in the methyl group. The dipole moments of ethylene oxide and trimethylene oxide in the vapour phase are 1·91 and 1·94 D respectively.[12] The C–O bonds are bent considerably in these molecules, and their calculated bond moments have no general significance. The COC angle in trimethyl oxide[10] has been determined as 94·5° ± 3°, though the bonds are probably slightly bent; in tetrahydrofuran the COC angle would be 102° if the CCC angles had their normal tetrahedral value: and 106° in 1,3-dioxolan.

The dipole moment of 1,3-dioxolan does not seem consistent with the results for the other cyclic ethers, yet it was completely reproducible. The dipole moments of several alkyl substituted 1,3-dioxolans have been reported to lie[13] between about 1·1 and 1·3 D. The substituents however were mainly in position 2, where the induced moments would lower the dipole moment. It is rather unlikely that the molecule is non-planar, but since the C–O bonds are about 0·11 Å shorter than C–C bonds the OCO angle must be greater than 109·5°; a OCO angle of 120° would give a C–O bond moment of about 1·72 D in much better agreement with the other values of Table 5.

TABLE 5.

	μ (D) at COC angles				
Compound	90°	94·5°	102°	106°	109·5°
C_3H_6O (13)	1·61	1·67			
C_4H_8O (14)		1·57	1·69	1·77	1·84
$C_5H_{10}O$ * (15)		1·40	1·51	1·57	1·64
$C_3H_6O_2$ (16)			2·31	2·31	2·32
$(CH_3)_2O$		1·25	1·33	1·37	1·42

* The results for this molecule depend only slightly on the extent to which its structure departs from the chair conformation of cyclohexane, with all the bond angles 109·5°.

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† If ∠CSC is 109·5°, then $\mu_{CS} = 1{\cdot}52$ D if the moment of Me_2S is employed,[2] but 1·68 D from the dipole moment of $Pr^n{}_2S$ where a contribution from induced moments in the alkyl chains is included. A bond angle 5° smaller would imply C–S bond moments of 1·45 and 1·60 D respectively ($\mu_{\overset{+\rightarrow}{\mathrm{C-H}}} = 0{\cdot}30$ D).

[11] Stuart, *Z. Physik*, 1928, **51**, 490; Hibbert and Allen, *J. Amer. Chem. Soc.*, 1932, **54**, 4115; Angyal, Barclay, and Le Fèvre, *J.*, 1950, 3370.

[12] Gent, *J.*, 1957, 58.

[13] Otto, *J. Amer. Chem. Soc.*, 1937, **59**, 1590; Bergmann, Fischer, Zimkin, and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 213.

Methyl ether with a dipole moment of 1·29 D in the vapour phase, and 1·25 D in benzene solution,[14] has a low apparent C–O bond moment because of greatly reduced contributions from induced moments, and the same is true for diethyl and di-n-propyl ether.[14] The COC angle[15] in dimethyl ether is about 111° and the C–O bond moment in solution is consequently about 1·41 D; it appears that the apparent C–O moment in cyclic ethers, where the contributions from induced moments are clearly greater, is about 1·66 D.

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[14] Barclay and Le Fèvre, *J.*, 1952, 1643.
[15] Kimura and Kubo, *J. Chem. Phys.*, 1959, **30**, 151.