73. *Molecular Polarisability: the Anisotropy of the Carbon–Oxygen Link.*

By R. J. W. Le Fèvre, (Mrs.) A. Sundaram, and (in part) R. K. Pierens.

The longitudinal and transverse polarisabilities of the C–O bond have been redetermined *via* polarity and molar Kerr constant measurements on 1,3,5-trioxan. Values of $10^{23}b_{\rm L}^{\rm C-O} = 0{\cdot}089$ and $10^{23}b_{\rm T}^{\rm C-O} = 10^{23}b_{\rm V}^{\rm C-O} = 0{\cdot}046$ are recommended, and used in discussing the conformations of 1,4-dioxan, 1,3-dioxolan, ethylene carbonate, methylal, and 1,8-cineole.

The measurements here reported on trioxan have been made to confirm or amend the values for the longitudinal and transverse polarisabilities * of the C–O bond ($b_{\rm L}^{\rm C-O} = 0{\cdot}081$ and $b_{\rm T}^{\rm C-O} = 0{\cdot}039$, respectively) earlier deduced by Le Fèvre and Le Fèvre [1a] from paraldehyde, using the structural specifications listed by Allen and Sutton.[2] A check seemed desirable because Sutton, when editing details in a later complication (see M 206 of ref. 3), has noted the possibility that the data in ref. 2 were drawn from a mixture of forms, and not from the isomer having all its methyl groups disposed equatorially, as presumed in ref. 2. Trioxan (M 151 of ref. 3) is free from such doubts.

It is now found, however, that although the estimates of $b_{\rm L}^{\rm C-O}$ and $b_{\rm T}^{\rm C-O}$ given in ref. 1(*a*) appear satisfactorily applicable to trioxan, they nevertheless correspond to an inadequate electronic polarisation for the C–O bond. Accordingly their replacement by $b_{\rm L}^{\rm C-O} = 0{\cdot}089$ and $b_{\rm T}^{\rm C-O} = 0{\cdot}046$ is now proposed; these, with other previously determined bond polarisabilities [4b] are utilised below in discussing the conformations of dioxan, dioxolan, ethylene carbonate, methylal, and cineole.

EXPERIMENTAL

Materials.—Trioxan (from Du Pont de Nemours and Co. Inc.), recrystallised twice from sodium-dried ether, had m. p. 62—63°. A commercial sample of 1,3-dioxolan (from Brotherton and Co. Ltd.) was distilled from sodium wire and the fraction having b. p. 78°/750 mm. (d_4^{20} 1·0600) was collected and stored in the dark. Ethylene carbonate, m. p. 32—34° (from the Jefferson Chemical Co. Inc., Texas), had m. p. 38° after fractional distillation (b. p. 236—237°/750 mm.). The 1,8-cineole was purified through its crystalline *o*-cresol complex. After final distillation (b. p. 176°/760 mm.) the liquid had $n_{\rm D}^{20}$ 1·4584 and d_4^{20} 0·9251; this stock was kept over sodium wire until required. Methylal was prepared as described by Fischer and Giebe;[5] dehydration by sodium and distillation gave material with b. p. 42·5°/760 mm., d_4^{20} 0·86012, and $n_{\rm D}^{20}$ 1·3534.

Techniques, Apparatus, Symbols, etc.—These have been described previously.[1a-c,4b] Symbols and equations used in calculating results from observational data have recently been summarised in ref. 6. The procedures for purifying benzene and carbon tetrachloride for use as solvents are also noted in the refs. just quoted. Results are given in the usual form in Tables 1 and 2. Table 1 is based on the following values at 25° for $n_{\rm D}$, d, ε, and B (for Na light) respectively, when $w_2 = 0$: 1·4973, 0·87378, 2·2725, and $0{\cdot}410 \times 10^{-7}$ for benzene, and 1·4575, 1·5845, 2·2270, and $0{\cdot}070 \times 10^{-7}$ for carbon tetrachloride,

---

* Polarisabilities of bonds or molecules are quoted throughout this paper in 10^{-23} c.c. units.

[1] Le Fèvre and Le Fèvre, (*a*) *J.*, 1956, 3549; (*b*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*c*) Chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, p. 2459.

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

[3] "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. Sutton, *Chem. Soc. Spec. Publ.* No. 11, 1958.

[4] Le Fèvre, (*a*) *Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (*b*) "Dipole Moments," Methuen, London, 3rd edn., 1953, Chap. 2.

[5] Fischer and Giebe, *Ber.*, 1897, **30**, 3054.

[6] Le Fèvre and Sundaram, *J.*, 1962, 1494.

TABLE 1.

Incremental values of n, n^2, d, ε, and B for solutions at 25°.

Solute: 1,3,5-*Trioxan*. *Solvent*: *Carbon tetrachloride*.

10^5w_2	$-10^4\Delta n$	$-10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
192	1	3	−94	202	−6
476	3	9	−253	493	−14
709	4	12	−375	747	−22
927	5	15	−498	976	−28
1376	8	23	−739	1458	−43
1686	10	29	−883	1798	−49
2048	12	35	−1052	2193	−63
2869	17	50	−1479	3120	−89
4131	26	76	−2116	4612	−128
5770	36	105	−2928	6714	−181
7843	—	—	—	—	−241

Whence $\sum\Delta n/\sum w_2 = -0{\cdot}060$;
$\sum\Delta n^2/\sum w_2 = -0{\cdot}177$;
$-\Delta d = 0{\cdot}5268w_2 - 0{\cdot}336w_2^2$;
$\Delta\varepsilon = 10{\cdot}32w_2 + 21{\cdot}92w_2^2$;
$\sum\Delta B/\sum w_2 = -3{\cdot}08 \times 10^{-7}$.

Solute: *Dioxolan*. *Solvent*: *Benzene*.

10^5w_2	$-10^4\Delta n$	$-10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
4426	36	106	700	1112	19
6789	55	162	1090	1705	—
8703	71	209	1420	2206	37
11,679	97	285	1905	2997	50
13,979	117	344	2319	3620	—
15,384	130	382	2576	4006	67
17,204	146	428	2855	4511	—
19,284	164	481	3205	5098	85
22,371	—	—	—	—	95
26,421	—	—	—	—	116

Whence $-\Delta n = 0{\cdot}0793w_2 + 0{\cdot}0312w_2^2$;
$-\Delta n^2 = 0{\cdot}2345w_2 + 0{\cdot}0816w_2^2$;
$\Delta d = 0{\cdot}1594w_2 + 0{\cdot}0395w_2^2$;
$\Delta\varepsilon = 2{\cdot}449w_2 + 1{\cdot}009w_2^2$;
$10^7\Delta B = 0{\cdot}4241w_2 + 0{\cdot}049w_2^2$.

Solute: *Cineole*. *Solvent*: *Carbon tetrachloride*.

10^5w_2	$-10^4\Delta n$	$-10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
4541	−2	−5	−5015	1306	−26
7127	−2	−5	−7697	2015	−42
9860	−3	−8	−10,402	2736	−58
13,977	−5	−14	−14,379	3782	−84
18,124	−6	−17	−18,130	4822	−110
23,052	−7	−20	−22,358	5866	−141

Whence $\sum\Delta n/\sum w_2 = 0{\cdot}003_3$;
$\sum\Delta n^2/\sum w_2 = 0{\cdot}009_0$;
$-\Delta d = 1{\cdot}1236w_2 - 0{\cdot}6712w_2^2$;
$\Delta\varepsilon = 2{\cdot}961w_2 - 1{\cdot}7715w_2^2$;
$-\Delta B = 0{\cdot}5758w_2 + 0{\cdot}1609w_2^2$.

Solute: *Methylal*. *Solvent*: *Carbon tetrachloride*.

10^5w_2	$-10^4\Delta n$	$-10^4\Delta n^2$	$10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
7027	128	365	−8637	528	−1·0
9397	169	481	−11,360	724	−1·3
12,025	234	664	−15,532	930	−1·9
14,272	259	735	−16,322	1120	−2·2

Whence $\sum\Delta n/\sum w_2 = -0{\cdot}1807$;
$\sum\Delta n^2/\sum w_2 = -0{\cdot}5135$;
$\Delta d = -1{\cdot}3162w_2 + 1{\cdot}1112w_2^2$;
$\Delta\varepsilon = 0{\cdot}7397w_2 + 0{\cdot}1286w_2^2$;
$\sum\Delta B/\sum w_2 = -0{\cdot}0146 \times 10^{-7}$.

Solute: *Ethylene carbonate*. *Solvent*: *Benzene*.

10^5w_2	296	1000	1415	1937	2508	2912
$-10^4\Delta n$	1	3	4	6	8	9
$-10^4\Delta n^2$	3	9	12	18	24	27

Whence $\sum\Delta n/\sum w_2 = -0{\cdot}0308$; $\sum\Delta n^2/\sum w_2 = -0{\cdot}0924$.

10^5w_2	296	1415	1569	1937	2508	2912
$10^5\Delta d$	104	496	502	675	875	1013

Whence $\sum\Delta d/\sum w_2 = 0{\cdot}3430$.

10^5w_2	151	178	210	263	302	330	935	1220
$10^4\Delta\varepsilon$	462	551	638	806	903	990	2785	3612

Whence $\sum\Delta\varepsilon/\sum w_2 = 29{\cdot}94$.

10^5w_2	35	147	342	538	711	772	951	997	1232
$10^{10}\Delta B$..............	9	41	96	149	199	208	256	272	320

Whence $\sum\Delta B/\sum w_2 = 27{\cdot}07 \times 10^{-7}$.

TABLE 2.

Total polarisations and molar Kerr constants at infinite dilution, molecular refractions, and dipole moments calculated from Table 1.

Solute	$(\alpha\varepsilon_1)_{w_2=0}$	$(\beta)_{w_2=0}$	$\gamma' n_1^2$	$_\infty P$ (c.c.)	R_D obsd. (c.c.)	μ (D) *	γ	δ	$10^{12}\ _\infty({}_mK_2)$
1,3,5-Trioxan †	10·32	−0·3325	−0·177	120·5	18·9	$2{\cdot}20_7$	−0·040	−44·00	$-32{\cdot}0_5$
Dioxolan ‡	$2{\cdot}44_9$	0·1824	$-0{\cdot}234_5$	54·7	17·0	$1{\cdot}34_3$	−0·053	1·034	4·28
Ethylene carbonate ‡	29·94	0·3925	−0·0924	514·1	16·4	4·93	−0·021	66·02	350·5
Cineole †	$2{\cdot}96_1$	−0·7091	$0{\cdot}009_0$	96·5	45·4	$1{\cdot}54_4$	0·002	$-8{\cdot}22_6$	−9·14
Methylal †	$0{\cdot}739_7$	−0·8307	$-0{\cdot}513_5$	31·5	19·6	$0{\cdot}72_9$	−0·124	−0·209	$0{\cdot}79_5$

* Calc. by taking $_DP = 1{\cdot}05R_D$. † Solvent: carbon tetrachloride. ‡ Solvent: benzene.

DISCUSSION

Dipole Moments.—Table 3 summarises previous estimates of μ for each of the six solutes here considered; to assist comparison with Tables 1 and 2, the values recorded for the total and distortion polarisations are also quoted. Our $_{\infty}P_2$ for trioxan is *ca.* 5 c.c. greater than that measured (in benzene) by Calderbank and Le Fèvre,[8] and the moment deduced is accordingly 0·05 D greater. Of the three previous determinations of μ for ethylene carbonate, that by Kempa and Lee [12] is closest to the 4·9 D of Table 2. Our μ for dioxalan is definitely below that published by Cumper and Vogel,[9] who however give no details of their material beyond noting it as a high-grade commercial product which was " extensively purified." The disagreement may be due to traces of water, for we find that dioxolan is difficult to preserve anhydrous and that its absorption in the 3500 cm.$^{-1}$ infrared region has a roughly linear relation to the $\alpha\varepsilon_1$ value exhibited by the corresponding solution; $\alpha\varepsilon_1$ of $2{\cdot}44_9$ given in Table 2 corresponds to a sample with no hydroxyl absorption. The $_{\infty}P_2$ of cineole in carbon tetrachloride exceeds that in benzene by only 0·7 c.c.; were $_{\mathrm{D}}P = R_{\mathrm{D}} = 45{\cdot}4$ c.c., the moments in these media would be 1·58 and 1·57, respectively; as a vapour,[13] over the range 200—300°, cineole has μ 1·58 D. For methylal, the $_{\infty}P_2$'s in n-hexane and carbon tetrachloride are 30·6 and 31·5 c.c., respectively; either value gives an apparent moment of *ca.* 0·7 D, suggesting a similarity of conformations in both solvents. Nevertheless, the flexibility of methylal is displayed by the polarisation–temperature studies on the gas by Kubo *et al.*,[15] which show the moment to rise progressively from 0·74 D at 34° to 1·13 D at 199°.

Anisotropy of Polarisability of the C–O *Link.*—The observed molar Kerr constant of trioxan is negative ($-32{\cdot}0_5 \times 10^{-12}$); all physical evidence [3,7,8,16,17] to date is consistent with a " chair " configuration for this molecule; therefore, the two triangles formed by joining the O ···· O ······ O and the C ····· C ······ C centres will lie in parallel planes. If the O–C–O and C–O–C angles are the same (they are quoted in ref. 3 as 110° ± 1° and 110° ± 2°, respectively), one of the three principal molecular semi-axes of polarisability (namely, b_3) and the direction of action of the molecular resultant dipole moment (μ_{res}) should, by symmetry, be perpendicular to the planes of these triangles with the remaining two axes (b_1 and b_2), of course, parallel to them. Further, also because of symmetry, b_1 is equal to b_2. The difference $b_1 - b_3$ can be obtained, by means of the usual equations,[1b,c] from the observed $_{\infty}({}_{\mathrm{m}}K_2)$ and μ_{res}, while the sum $2b_1 + b_3$ should be accessible through

TABLE 3.

Previous estimates of dipole moments, polarisations, etc.

Solute	Temp.	Medium or state	Moment (D)	$_{\infty}P_2$ c.c.	$_{\mathrm{D}}P$ c.c. used	Ref.
1,3,5-Trioxan	30°	C_6H_6	2·18	114·4	18·8	7
	25	,,	2·16	115·3	19·3	8
Dioxolan	25	,,	1·47	61·28	17·15	9
Ethylene carbonate	25	,,	4·80			10
	25	,,	4·60	Not quoted		11
	25	,,	4·87	510·2	17·8	12
Cineole	25	,,	1·57	95·8	45·5	13
Methylal	25	*n*-C_6H_{14}	0·67	30·56	21·27	14

---

[7] Maryott and Acree, *J. Res. U.S. Nat. Bur. Stds.*, 1944, **33**, 71.

[8] Calderbank and Le Fèvre, *J.*, 1949, 199.

[9] Cumper and Vogel, *J.*, 1959, 3521.

[10] Arbuzov and Shavsha, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 1045.

[11] Longster and Walker, *Trans. Faraday Soc.*, 1953, **49**, 228.

[12] Kempa and Lee, *J.*, 1958, 1936.

[13] Freeman, Le Fèvre, and Maramba, *J.*, 1952, 1649.

[14] Uchida, Kurita, and Kubo, *J. Polymer Sci.*, 1956, **19**, 365.

[15] Kubo, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 1936, **29**, 122.

[16] Mizushima, Morino, and Kubo, *Phys. Z.*, 1937, **38**, 459.

[17] Ramsay, *Trans. Faraday Soc.*, 1948, **44**, 289.

refractivity data. Numerically $b_1 - b_3$ emerges from experiment as $\pm 0{\cdot}059_7 \times 10^{-23}$, but $2b_1 + b_3$ cannot be estimated with certainty in this case because the necessity of working with solutions makes unreliable any attempt to secure the electronic polarisation, ${}_{\mathrm{E}}P = R_\infty$, by extrapolating data for R_λ against λ to R_∞. Alternatively, therefore, we take ${}_{\mathrm{E}}P$ as either (*a*) $0{\cdot}95\ R_{\mathrm{D}} = 17{\cdot}955$ c.c., or (*b*) as the sum ($18{\cdot}80_4$ c.c.) of the bond electronic polarisations listed by Le Fèvre and Steel.[18] Since $2b_1 + b_3 = 0{\cdot}11891 \times 10^{-23}{}_{\mathrm{E}}P$, the total polarisabilities of trioxan are (*a*) $2{\cdot}135 \times 10^{-23}$ or (*b*) $2{\cdot}2360 \times 10^{-23}$; the semi-axes for this molecule accordingly appear as $b_1 = 0{\cdot}732 \times 10^{-23}$ and $b_3 = 0{\cdot}672 \times 10^{-23}$ through (*a*), or $b_1 = 0{\cdot}765 \times 10^{-23}$ and $b_3 = 0{\cdot}705_5 \times 10^{-23}$ through (*b*).

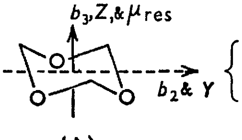
Now, using the bond lengths and angles given in ref. 3, together with the polarisability of the C–H link as in refs. 1 and 4(*a*), but with $b_{\mathrm{L}}^{\mathrm{C-O}}$ and $b_{\mathrm{T}}^{\mathrm{C-O}}$ as unknowns, enables simultaneous equations to be written for b_1(trioxan) and b_3(trioxan); these yield solutions as follows:

	$10^{23}b_{\mathrm{L}}^{\mathrm{C-O}}$	$10^{23}b_{\mathrm{T}}^{\mathrm{C-O}}$
From source (*a*)	0·084	0·040
,, (*b*)	0·089	0·046

The results from (*a*) are close to those ($0{\cdot}081$ and $0{\cdot}039 \times 10^{-23}$) originally deduced by Le Fèvre and Le Fèvre,[1a] a fact illustrated by Table 4 in which b_1 and b_3 are computed for the "chair" model of trioxan by using the old values. The ${}_{\mathrm{m}}K$ calc. is $-30{\cdot}7 \times 10^{-12}$, against the $-32{\cdot}0_5 \times 10^{-12}$ observed. [Table 4 includes calculations for a boat and a planar form; for each, an algebraically *positive* molar Kerr constant is forecast; the fact that the measured ${}_\infty({}_{\mathrm{m}}K_2)$ is actually more, not less, negative than $-30{\cdot}7 \times 10^{-12}$ supports the allocation of a chair-type configuration to trioxan as a solute and leaves no grounds for considering a boat–chair equilibrium or mixture.]

Table 4.

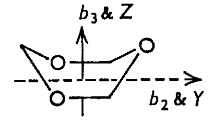
Polarisability semi-axes and molar Kerr constants computed for chair, boat, and planar models of trioxan.



(A)

Model A.*

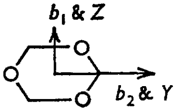
$$\left\{\begin{array}{l} b_1\dagger = 0{\cdot}721_1 \\ b_2 = 0{\cdot}721_1 \\ b_3 = 0{\cdot}663_9 \end{array}\right. \quad \left.\begin{array}{l} \mu_1\ddagger = 0 \\ \mu_2 = 0 \\ \mu_3 = 2{\cdot}21 \end{array}\right\} {}_{\mathrm{m}}K \text{ calc.} = -30{\cdot}7\S$$



(B)

Model B.*

$$\left\{\begin{array}{l} b_1 = 0{\cdot}730_7 \\ b_2 = 0{\cdot}739_0 \\ b_3 = 0{\cdot}636_4 \end{array}\right. \quad \left.\begin{array}{l} \mu_1 = 0 \\ \mu_2 = 1{\cdot}81 \\ \mu_3 = 1{\cdot}27 \end{array}\right\} {}_{\mathrm{m}}K \text{ calc.} = +2{\cdot}9$$



(C)

Model C.*

$$\left\{\begin{array}{l} b_1 = 0{\cdot}744 \\ b_2 = 0{\cdot}744 \\ b_3 = 0{\cdot}618 \end{array}\right. \quad \left.\begin{array}{l} \mu_1 = 0 \\ \mu_2 = 0 \\ \mu_3 = 0 \end{array}\right\} {}_{\mathrm{m}}K \text{ calc.} = +0{\cdot}8$$

* In the first two models the planes of the end triangles meet the central plane at 126·6°. † b_1, b_2, b_3 are in 10^{-23} c.c. units. ‡ Moment components are in D units. § Molar Kerr constants are in 10^{-12} units.

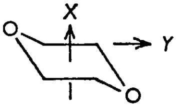
It is now suggested that of the three sets (*i.e.*, those with $10^{23}b_{\mathrm{L}}^{\mathrm{C-O}} = 0{\cdot}081$, $0{\cdot}084$, or $0{\cdot}089$, respectively) of polarisabilities for the C–O bond, the last is to be preferred.

[18] Le Fèvre and Steel, *Chem. and Ind.*, 1961, 670.

TABLE 5.

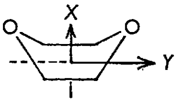
Polarisability semi-axes, moment components, etc., calculated for four conformations of 1,4-dioxan.*

Model: *chair* (D).



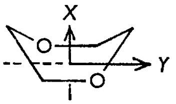
		Direction cosines with				
		X	Y	Z		
(0) †	$b_1 = 0{\cdot}759_2$	0·9778	0·2096	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 0{\cdot}62$
	$b_2 = 0{\cdot}887_0$	−0·2096	0·7778	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}832_6$	0	0	1	$\mu_3 = 0$	
(*a*) †	$b_1 = 0{\cdot}764_5$	0·9751	0·2215	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 0{\cdot}62_5$
	$b_2 = 0{\cdot}982_5$	−0·2215	0·9751	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}841_8$	0	0	1	$\mu_3 = 0$	
(*b*) †	$b_1 = 0{\cdot}787_2$	0·9940	0·1097	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 0{\cdot}61_0$
	$b_2 = 0{\cdot}913_3$	−0·1097	0·9940	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}866_3$	0	0	1	$\mu_3 = 0$	

Model: *Sym. boat* (E).‡



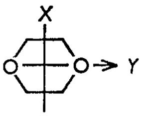
(0)	$b_1 = 0{\cdot}759_8$	1	0	0	$\mu_1 = 2{\cdot}13$	$_{\mathrm{m}}K = -49{\cdot}4$
	$b_2 = 0{\cdot}886_4$	0	1	0	$u_2 = 0$	
	$b_3 = 0{\cdot}832_6$	0	0	1	$\mu_3 = 0$	
(*a*)	$b_1 = 0{\cdot}765_6$	1	0	0	$\mu_1 = 2{\cdot}13$	$_{\mathrm{m}}K = -50{\cdot}0$
	$b_2 = 0{\cdot}891_4$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}841_8$	0	0	1	$\mu_3 = 0$	
(*b*)	$b_1 = 0{\cdot}788_7$	1	0	0	$\mu_1 = 2{\cdot}13$	$_{\mathrm{m}}K = -49{\cdot}7$
	$b_2 = 0{\cdot}911_8$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}866_3$	0	0	1	$\mu_3 = 0$	

Model: *unsym. boat* (F).‡



(0)	$b_1 = 0{\cdot}772_8$	1	0	0	$\mu_1 = 1{\cdot}07$	$_{\mathrm{m}}K = -9{\cdot}7$
	$b_2 = 0{\cdot}8312$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}874_8$	0	0	1	$\mu_3 = 0$	
(*a*)	$b_1 = 0{\cdot}777_6$	1	0	0	$\mu_1 = 1{\cdot}07$	$_{\mathrm{m}}K = -10{\cdot}0$
	$b_2 = 0{\cdot}839_8$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}881_4$	0	0	1	$\mu_3 = 0$	
(*b*)	$b_1 = 0{\cdot}801_3$	1	0	0	$\mu_1 = 1{\cdot}07$	$_{\mathrm{m}}K = -9{\cdot}9$
	$b_2 = 0{\cdot}861_5$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}904_0$	0	0	1	$\mu_3 = 0$	

Model: *Planar* (G).



(0)	$b_1 = 0{\cdot}851_4$	1	0	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 1{\cdot}3_2$
	$b_2 = 0{\cdot}904_8$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}722_8$	0	0	1	$\mu_3 = 0$	
(*a*)	$b_1 = 0{\cdot}861_4$	1	0	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 1{\cdot}3_6$
	$b_2 = 0{\cdot}910_6$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}726_8$	0	0	1	$\mu_3 = 0$	
(*b*)	$b_1 = 0{\cdot}882_3$	1	0	0	$\mu_1 = 0$	$_{\mathrm{m}}K = 1{\cdot}3_3$
	$b_2 = 0{\cdot}933_7$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}750_8$	0	0	1	$\mu_3 = 0$	

* See footnotes to Table 4 for units. † To indicate which C–O polarisabilities are used: (0) = original values from ref. 1(*a*), (*a*) = values from source (*a*) above, (*b*) values from source (*b*) above. ‡ Moments calc. by using $\mu_{\mathrm{C-O}} = 1{\cdot}14_5$ D, and assuming all interbond angles are *ca.* 109·5°.

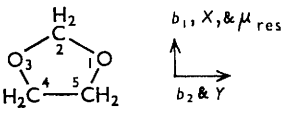
Previously, when relating the longitudinal polarisabilities and stretching frequencies of links, Le Fèvre[19] noted that a $b_{\rm L}^{\rm C-O}$ of *ca.* 0·09 × 10^{-23}, at least, seemed more in place among results for other bonds than one of *ca.* 0·08 × 10^{-23}; moreover, the total (× 10^{23}), 0·081 + 2 × 0·039 = 0·159, corresponds to an ${}_{\rm E}P^{\rm C-O}$ of 1·337 c.c. which is only 0·92 of $R_{\rm D}^{\rm C-O}$ of 1·46 c.c. given by Vogel *et al.* for acetals[20] and only 0·87 of the 1·54 c.c. quoted for ethers.[20] The semi-axes now recommended for C–O (*viz.*, $b_{\rm L}^{\rm C-O} = 0{\cdot}089$, $b_{\rm T}^{\rm C-O} = b_{\rm V}^{\rm C-O} = 0{\cdot}046 \times 10^{-23}$) agree with an ${}_{\rm E}P$ of 1·52 c.c., *i.e.*, $0{\cdot}98_7$ of $R_{\rm D}^{\rm C-O}$.

Since neither the $b_{\rm L}^{\rm C-O}/b_{\rm T}^{\rm C-O}$ ratios nor the $b_{\rm L}^{\rm C-O} - b_{\rm T}^{\rm C-O}$ differences are much affected by these changes, molar Kerr constants calculated *a priori* for structures involving C–O bonds will not be very sensitive to the data adopted for $b_{\rm L}^{\rm C-O}$ and $b_{\rm T}^{\rm C-O}$; the point is illustrated by the examples in Tables 5 and 6 below.

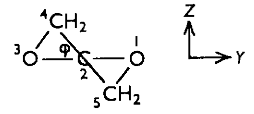
The Conformation of 1,4-*Dioxan.*—Electron diffraction studies[21] by Sutton and Brockway, Kimura, and Aoki, and others, suggest that this molecule has a " chair " configuration in which the C–C–O and C–O–C angles are nearly the same (109° ± 1° and 109·5° ± 1·5°, respectively); such a model should theoretically be non-polar. However the literature[8, 22-24] lists values ranging from 0 to 0·45 D; either, therefore, the atomic polarisation has been sometimes underestimated, or—in the light of the high-temperature dielectric constant effects noted by Gibbs and Armstrong *et al.*[23] with dioxan vapour—this ether as a liquid or solute is an equilibrium of " chair " and " boat " forms. Against the last view is Malherbe and Bernstein's careful reinvestigation[25] of the Raman and infrared spectra of liquid dioxan, the vibrations in which could be assigned on the basis alone of the (" chair ") point group C_{2h}, and also the apparent constancy of the total polarisation of this material from 0·7° below its m. p. to at least 20° above.[26]

To investigate the matter further the principal axes of the polarisability ellipsoids of the four possible conformations (" chair," symmetrical " boat," unsymmetrical " boat," and planar forms) have been calculated (Table 5).

It is seen that of the calculated ${}_{\rm m}K$'s, only those for the " chair " and the planar form are algebraically positive. From the following experimental data for dioxan at 25°: $\varepsilon = 2{\cdot}2090$; $n_{\rm D} = 1{\cdot}4202$; $d = 1{\cdot}0280$; $B_{\rm D} = 0{\cdot}068 \times 10^{-7}$; the molar Kerr constant for liquid dioxan follows as $+1{\cdot}0 \times 10^{-12}$, *i.e.*, positive and slightly greater than the values for the first isomer reported in Table 5. Thus the likelihood of either of the other two non-planar forms being present at room temperature seems small. The flat model, although allowed by present results, is, of course, rejected on the grounds that in it H · · · H repulsions and valency angle strains will exceed those in the " chair " structure.



(I)



(II)

Conformations of 1,3-*Dioxolan and Ethylene Carbonate.*—The infrared and Raman spectra[27] of 1,3-dioxolan have indicated a non-planar structure; an earlier reference

---

[19] Le Fèvre, *Proc. Chem. Soc.*, 1959, 363.

[20] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

[21] Sutton and Brockway, *J. Amer. Chem. Soc.*, 1935, **57**, 473; Kimura and Aoki, *J. Chem. Soc. Japan*, 1951, **72**, 169.

[22] Wesson, " Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

[23] Gibbs, *Discuss. Faraday Soc.*, 1951, **10**, 122; Armstrong, Le Fèvre, and Yates, *Austral. J. Chem.*, 1958, **11**, 147.

[24] Marchal and Lapp, *J. Polymer Sci.*, 1958, **27**, 571.

[25] Malherbe and Bernstein, *J. Amer. Chem. Soc.*, 1952, **74**, 4408.

[26] Yasumi and Shirai, *Bull. Chem. Soc. Japan*, 1955, **28**, 193; cf. also Vaughan, *Phil. Mag.*, 1939, **27**, 669.

[27] Barker, Bourne, Pinkard, and Whiffen, *J.*, 1959, 802.

(M 151 of ref. 3) also suggested such a form, with all angles approximately 108°. Neither of these sources states the degree of puckering of the ring. Although intervalency angles of *ca.* 108° make feasible a flat structure (I), repulsions between hydrogen atoms on neighbouring carbon atoms should tend to cause non-planarity. Several non-planar models are possible; of these, only type (II), in which the four C–H bonds are staggered, is considered here. The triangle $O_{(1)}$–$C_{(2)}$–$O_{(3)}$ is taken as the plane containing the arbitrary axes X and Y, with Y parallel to the $O_{(3)} \cdots O_{(1)}$ line; the $C_{(4)}$–$C_{(5)}$ bond is twisted through $\phi°$ so that these carbon atoms are respectively above and below their projections in the XY plane. It follows that the line joining the mid-point of $C_{(4)}$–$C_{(5)}$ to the centre of $C_{(2)}$ is parallel to the X-axis and to the direction of action of the resultant moment (μ_{res}).

Relevant calculations are in Table 6. The observed $_mK$ is $4{\cdot}2_8 \times 10^{-12}$ (Table 2).

TABLE 6.

Polarisability semi-axes, moment components, etc., for two models of 1,3-dioxolan.*

Planar model (I)

		Direction cosines with				
		X	Y	Z		
(0) †	$b_1 = 0{\cdot}672_5$	1	0	0	$\mu_1 = 1{\cdot}34_3$	$_mK = 8{\cdot}32$
	$b_2 = 0{\cdot}701_6$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}567_4$	0	0	1	$\mu_3 = 0$	
(*b*) †	$b_1 = 0{\cdot}702_5$	1	0	0	$\mu_1 = 1{\cdot}34_3$	$_mK = 8{\cdot}59$
	$b_2 = 0{\cdot}731_5$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}595$	0	0	1	$\mu_3 = 0$	

Non-planar model (II; $\phi = 48°$)

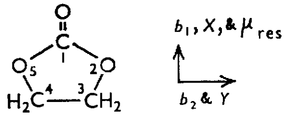
		X	Y	Z		
(0)	$b_1 = 0{\cdot}659_8$	1	0	0	$\mu_1 = 1{\cdot}34_3$	$_mK = 3{\cdot}6_5$
	$b_2 = 0{\cdot}672_6$	0	0·8920	0·4522	$\mu_2 = 0$	
	$b_3 = 0{\cdot}609_1$	0	−0·4522	0·8920	$\mu_3 = 0$	
(*b*)	$b_1 = 0{\cdot}689_4$	1	0	0	$\mu_1 = 1{\cdot}34_3$	$_mK = 4{\cdot}00$
	$b_2 = 0{\cdot}692_8$	0	0·9715	0·2368	$\mu_2 = 0$	
	$b_3 = 0{\cdot}646_8$	0	−0·2368	0·9715	$\mu_3 = 0$	

* Units as above. † See footnote to Table 5.

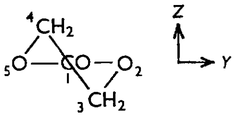
For the planar form, the $_mK$ calc. is *ca.* 9×10^{-12}, but for a version of (II) with $\phi = 48°$ (found by trial and error) the $_mK$ calc. is in agreement with experiment.

A non-planar ring has also been suggested for ethylene carbonate; ref. 3 (M 148) shows the $C_{(3)}$–$C_{(4)}$ bond in (III) rotated by 20° in the YZ plane, thus giving model (IV). The angles adopted for (III) are: at $C_{(1)}$ 112°, at $O_{(2)}$ and $O_{(5)}$ 110°, at $C_{(3)}$ and $C_{(4)}$ 104°; for (IV): at $C_{(1)}$ 111°, at $O_{(2)}$ and $O_{(5)}$ 109°, at $C_{(3)}$ and $C_{(4)}$ 102° (cf. ref. 3). Table 7 summarises calculations for form (III) and for form (IV) with $\phi = 20°$ or 72°; the larger value of ϕ is that required to bring the calculated $_mK$ to parity with that observed.

However, the degree of puckering when $\phi = 72°$ seems high and abnormal. (The molecule contains one usually trigonal carbon atom and is therefore already strained if the angle at $C_{(1)}$ is 111—112°; non-planarity will increase this strain. Hydrogen–hydrogen repulsions should not be expected to cause two C–H bonds to be staggered more than *ca.* 60°.) The difficulty in reconciling the observed with the calculated molar Kerr constants may be due to the use of ketonic polarisabilities as drawn [28] from acetone. The C=O group in ethylene carbonate is markedly different from that in acetone: it is



(III)



(IV)

---

[28] Le Fèvre, Le Fèvre, and Rao, *J.*, 1959, 2340.

shorter (1·15 compared with 1·22 Å),[3] and its infrared stretching absorption occurs at a higher frequency (1820—1830 compared with *ca.* 1720 cm.$^{-1}$).[29,30] We are aware that, as advised explicitly before (*e.g.*, ref. 1(*b*), p. 302, or ref. 4(*a*), p. 3), bond polarisabilities for use in a particular situation should be those deduced from as similar a situation as possible, yet to date no molecules with such unusual ketone groups have been studied from the present viewpoint. In the interim, therefore, we note that with $r = 1{\cdot}15$ Å and $\nu_{\rm str}$ (C=O) taken as 1825 cm.$^{-1}$, Le Fèvre's equation [19] indicates a $b_{\rm L}^{\rm C=O}$ around 0·18, *i.e.*, lower than the 0·230 found satisfactory hitherto with ketones.[31] The chief effect of diminishing $b_{\rm L}^{\rm C=O}$ will be to reduce the b_1's shown in Table 7. Because of the large $\mu_{\rm res}$, the $_{\rm m}K$'s calculated are sensitive to the term $2b_1 - b_2 - b_3$, and in the (*b*) sets for the planar and the $\phi = 20°$ model an alteration of $b_{\rm L}^{\rm C=O}$ from 0·23 to 0·20 leads to $_{\rm m}K$'s of 357 and 349 $\times$ 10^{-12}, respectively, the lower of these being close to that observed (Table 2).

TABLE 7.

Polarisability semi-axes, moment components, etc., for three models of ethylene carbonate.*

		Direction cosines with X	Y	Z		
	Planar model (III)					
(*b*) †	$b_1 = 0{\cdot}805_3$	1	0	0	$\mu_1 = 4{\cdot}93$	$_{\rm m}K = 480$
	$b_2 = 0{\cdot}742_7$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}513_0$	0	0	1	$\mu_3 = 0$	
	Non-planar model (IV; $\phi = 20°$)					
(*b*)	$b_1 = 0{\cdot}802_7$	1	0	0	$\mu_1 = 4{\cdot}93$	$_{\rm m}K = 469$
	$b_2 = 0{\cdot}736_4$	0	0·9985	0·0541	$\mu_2 = 0$	
	$b_3 = 0{\cdot}521_9$	0	−0·0541	0·9985	$\mu_3 = 0$	
	Non-planar model (IV; $\phi = 72°$)					
(*b*)	$b_1 = 0{\cdot}773_9$	1	0	0	$\mu_1 = 4{\cdot}93$	$_{\rm m}K = 351$
	$b_2 = 0{\cdot}678_4$	0	0·9954	0·0958	$\mu_2 = 0$	
	$b_3 = 0{\cdot}608_7$	0	−0·0958	0·9954	$\mu_3 = 0$	

* Units as above. † See footnote to Table 5

Conformation of 1,8-*Cineole.*—In the absence from the literature of structural details for this molecule, " Barton " models have been utilised. With C–C and C–O bond lengths of 1·54 and 1·42 Å, respectively, a form (V) appears in which intervalency angles (measured by hand) are $a = 109°$, $b = 110°$, $c = 112°$, $d = 66°$, and $e = 70°$. The eight hydrogen atoms associated with bonds 2 and 5 are eclipsed, but it seems possible to relieve this situation by twisting bonds 2, 5, and 8 by 15° with respect to the *AOB* line; two mirror-image variants (Va) and (Vb) are thus created. In (Va), on looking at the model along *AOB*, bonds 1, 6, and 9 are seen 7·5° clockwise, and bonds 3, 4, and 7 are 7·5° anticlockwise, to *OQ*, *OP*, and *OR* (the same description applies, of course, to (Vb), but with the words clockwise and anticlockwise interchanged). The point O is the centre of *AB*; *P*, *Q*, and *R* are the centres of bonds 5, 2, and 8; the lines *OP*, *OQ*, and *OR* meet at 120° at O. In (Va) or (Vb) angles are found as follow: a = 107°, b = 108°, c = 110°, d = 64°, and e = 68°. Arbitrary axes *OX*, *OY*, and *OZ* are chosen with *OX* along *AOB* and *OZ* along *OR*. The resultant moment then acts at 36° to *OZ* in the *ZOX* plane for structure (V), and slightly divergently from this plane for structures (Va) or (Vb) which accordingly have $\mu_{\rm OX} = 0{\cdot}860$, $\mu_{\rm OY} = 0{\cdot}135$, and $\mu_{\rm OZ} = 1{\cdot}275$ D. Calculations for cineole are in Table 8.

It is seen that the molar Kerr constant predicted for the conformation having staggered

---

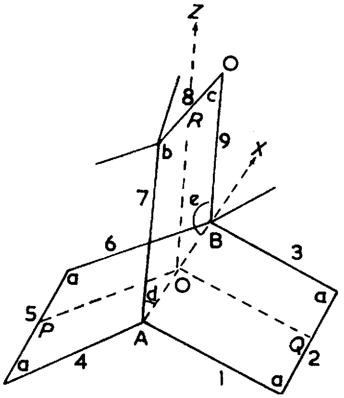
[29] Angell, *Trans. Faraday Soc.*, 1956, **52**, 1178.

[30] Hartwell, Richards, and Thompson, *J.*, 1948, 1436.

[31] Aroney, Izsak, and Le Fèvre, *J.*, 1961, 4148.

C–H links approaches the observed value ($-9{\cdot}1_4 \times 10^{-12}$) rather more closely than that corresponding to structure (V).

Conformation of Methylal.—With this solute problems are multiplied through the possibilities of internal rotations about the two inner C–O bonds. At first sight methylal might adopt an infinite number of conformations between the three extreme planar structures (VIa, b, and c). The dipole moments expected for these, with $\mu(\mathrm{Me_2O}) = 1{\cdot}32$ D, are 2·64, 0·9, and $1{\cdot}51_4$ D, respectively; the observed value at 25° is 0·73 D (Table 2), a fact which suggests (VIb) as more nearly appropriate than (VIa) or (VIc). However, scale models show that (VIb) cannot be fully planar for steric reasons, but that forms having the terminal methyl groups above and below the $\mathrm{O{\cdot}CH_2{\cdot}O}$ plane are feasible.



(V)

TABLE 8.

Polarisability semi-axes, moment components, etc.,* for two † models of 1,8-cineole.

Model (V)

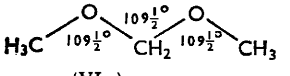
		Direction cosines with X	Y	Z		
(*b*) ‡	$b_1 = 1{\cdot}835$	1	0	0	$\mu_1 = 0{\cdot}90_8$	${}_{\mathrm{m}}K = -10{\cdot}8$
	$b_2 = 1{\cdot}804$	0	1	0	$\mu_2 = 0$	
	$b_3 = 1{\cdot}713$	0	0	1	$\mu_3 = 1{\cdot}24_9$	

Models (Va) and (Vb)

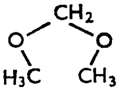
		X	Y	Z		
(*b*)	$b_1 = 1{\cdot}831$	0·9980	−0·0143	0·0620	$\mu_1 = 0{\cdot}93_5$	${}_{\mathrm{m}}K = -9{\cdot}2_7$
	$b_2 = 1{\cdot}806$	0·0061	0·9989	0·0470	$\mu_2 = 0{\cdot}20_0$	
	$b_3 = 1{\cdot}715$	−0·0633	−0·0450	0·9970	$\mu_3 = 1{\cdot}21_2$	

* Units as above. † Forms (Va) and (Vb) cannot be distinguished by either μ_{res} or ${}_{\mathrm{m}}K$. ‡ See footnote to Table 5.

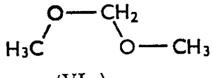
Table 9 reports calculations carried through for the above three structures and for four non-planar variants of them: (VId—f) in which the O–$\mathrm{CH_3}$ bonds are twisted in opposite directions from their positions in the planar form (VIb) by 30°, 60°, and 90°, respectively, and (VIg) produced by similar 60° twists applied to (VIa). The O–C–O and C–O–C valency angles are taken as 109·5° from the electron-diffraction study by Aoki.[32]



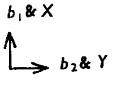
(VIa)



(VIb)



(VIc)



---

[32] Aoki, *J. Chem. Soc. Japan*, 1953, **74**, 110.

None of these seven conformations will exactly satisfy both the moment and the molar Kerr constant, although (VId) is nearest to doing so. Of course, mixtures can be devised to meet such a requirement [*e.g.*, 42% of (VId) and of (VIf) with 10·7% of (VIe) and 5·3% of (VIc) should show an ${}_{\mathrm{m}}K$ of $0{\cdot}8 \times 10^{-12}$ and a μ of 0·73 D], but since the uncertainty of measurement of ${}_{\mathrm{m}}K$'s, as of μ's, increases with the smallness of these quantities it seems scarcely justified to invoke forms outside the range (VId—f) merely to adjust ${}_{\mathrm{m}}K$ by $1{\cdot}0 \times 10^{-12}$ or μ by 0·1 D. The conformations just mentioned thus resemble the gauche-type structures already proposed for methylal by Kubo *et al.*,[14-16] and, qualitatively at least, are harmoniously related to the helical arrangement described by Hengstenberg[33] and Sauter[33] for (solid) polyoxymethylene.

TABLE 9.

Polarisability semi-axes, moment components, etc.,* for four conformations of methylal.

		Direction cosines with †				
		X	Y	Z		
			Model (VIa)			
(*b*) ‡	$b_1 = 0{\cdot}752_6$	1	0	0	$\mu_1 = 2{\cdot}64$	${}_{\mathrm{m}}K = -0{\cdot}34_5$
	$b_2 = 0{\cdot}811_4$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}696$	0	0	1	$\mu_3 = 0$	
			Model (VIb)			
(*b*)	$b_1 = 0{\cdot}804_6$	1	0	0	$\mu_1 = 0{\cdot}9$	${}_{\mathrm{m}}K = +7{\cdot}3$
	$b_2 = 0{\cdot}759_4$	0	1	0	$\mu_2 = 0$	
	$b_3 = 0{\cdot}696$	0	0	1	$\mu_3 = 0$	
			Model (VIc)			
(*b*)	$b_1 = 0{\cdot}772$	1	0	0	$\mu_1 = 0$	${}_{\mathrm{m}}K = +15{\cdot}1$
	$b_2 = 0{\cdot}792$	0	1	0	$\mu_2 = 1{\cdot}51_4$	
	$b_3 = 0{\cdot}696$	0	0	1	$\mu_3 = 0$	
			Model (VId)			
(*b*)	$b_1 = 0{\cdot}784_5$	1	0	0	$\mu_1 = 0{\cdot}63$	${}_{\mathrm{m}}K = +2{\cdot}2_3$
	$b_2 = 0{\cdot}758_0$	0	0·9997	0·0216	$\mu_2 = 0$	
	$b_3 = 0{\cdot}717_5$	0	−0·0216	0·9997	$\mu_3 = 0$	
			Model (VIe)			
(*b*)	$b_1 = 0{\cdot}7443$	1	0	0	$\mu_1 = 0{\cdot}05$	${}_{\mathrm{m}}K = 0{\cdot}00_4$
	$b_2 = 0{\cdot}755_4$	0	0·8980	0·4399	$\mu_2 = 0$	
	$b_3 = 0{\cdot}760_3$	0	−0·4399	0·8980	$\mu_3 = 0$	
			Model (VIf)			
(*b*)	$b_1 = 0{\cdot}727_5$	1	0	0	$\mu_1 = 0{\cdot}75_4$	${}_{\mathrm{m}}K = -2{\cdot}2_8$
	$b_2 = 0{\cdot}742_8$	0	0·7891	0·6143	$\mu_2 = 0$	
	$b_3 = 0{\cdot}789_7$	0	−0·6143	0·7891	$\mu_3 = 0$	
			Model (VIg)			
(*b*)	$b_1 = 0{\cdot}731_2$	1	0	0	$\mu_1 = 1{\cdot}8$	${}_{\mathrm{m}}K = -11{\cdot}8$
	$b_2 = 0{\cdot}748_6$	0	0·8988	0·4384	$\mu_2 = 0$	
	$b_3 = 0{\cdot}780_2$	0	−0·4384	0·8988	$\mu_3 = 0$	

* Units as above. † Axes X, Y, and Z disposed as indicated alongside (VIa—c). ‡ See footnote to Table 5.

The award by the University of Sydney of an " A. E. and F. A. Q. Stephens " research scholarship to A. S. is gratefully acknowledged.

UNIVERSITY OF SYDNEY, N.S.W., AUSTRALIA.

[*Received, July* 17*th*, 1962.]

---

[33] Hengstenberg, *Ann. Phys.*, 1927, **84**, 245; Sauter, *Z. phys. Chem.*, 1932, *B*, **18**, 417; 1933, *B*, **21**, 186.