90. *Molecular Polarisability. The Conformations of 2,3-Diphenyl-1,4-dioxen and Some 2,3-Disubstituted 1,4-Dioxans as Solutes.*

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Polarisation and polarisability measurements, together with nuclear magnetic resonance (n.m.r.) spectra, show that the so-called *cis* 2,3-dichloro-1,4-dioxan, m. p. 52°, is actually the *trans*-compound and that the isomers of 2,3-diphenyl-1,4-dioxan with m. p. 46 and 132° are *cis* and *trans*, respectively. In all cases studied, the heterocyclic rings remain in a chair form. The n.m.r. spectrum of 2,3-diphenyl-1,4-dioxan of m. p. 132° indicates that, at room temperature, the rotation of the phenyl rings is hindered. The 1,4-dioxen ring in 2,3-diphenyl-1,4-dioxen appears to exist preferentially as a half-chair form.

THE conformations of saturated six-membered heterocyclic molecules have not been extensively investigated despite apparent similarities to the cyclohexane series. We have begun a systematic study of such compounds and here report details for some derivatives of 1,4-dioxan.

EXPERIMENTAL

Solutes, Methods, etc.—The solutes, *trans*-2,3-dibromo-1,4-dioxan, m. p. 73° (I), the 2,3-dichloro-1,4-dioxans, m. p. 30° (IIa) and 52° (IIb), 2,3-diphenyl-1,4-dioxen, m. p. 89° (III), the 2,3-diphenyl-1,4-dioxans, m. p. 46° (IVa) and 132° (IVb), and *trans-p*-dioxino[2,3-*b*]-*p*-dioxin (R.R.I. 1644) (the so-called 1,4:5,8-naphthodioxan), m. p. 134°, (V) were synthesized as described in refs. 1—3.

Details of apparatus, procedures, symbols, etc., involved with the polarisation and polarisability measurements, have been given before.[4] Nuclear magnetic resonance (n.m.r.) spectra were recorded on a Varian Associates A60 spectrometer operating at 60 Mc./sec. for 5—10% w/v solutions in deuteriochloroform containing tetramethylsilane as internal reference.

Polarisation, Polarisability Measurements, and Results.—These follow under the usual headings[4] as Tables 1 and 2. Equations used in passing from Table 1 to Table 2 are summarised in ref. 5.

The dipole moments now found confirm those recorded in refs. 6 and 7. No previously published data for the dipole moments of compounds (III), (IVa), and (IVb) can be located.

DISCUSSION

Previous Assignments.—Until recently, the configurational assignments for a number of 2,3-disubstituted 1,4-dioxans have been [3,6,8] as shown in Table 3. Among these assignments, only those for compounds (I) and (IIa) can be regarded as conclusive (*X*-ray diffraction studies[6] having provided evidence that (I) and (IIa) exist in conformations in which the rings are in chair forms and the substituents are diaxial). Theoretically, such conformations, taken as rigid, should not exhibit appreciable dipole moments. The experimental moment of 1·86 D for (I) and 1·67 D for (IIa) can be explained only by reasoning

[1] Dehn, *J. Org. Chem.*, 1958, **23**, 147.
[2] Broseken, Tellegen, and Henriquez, *Rec. Trav. chim.*, 1931, **50**, 909.
[3] (a) Summerbell and Lunk, *J. Amer. Chem. Soc.*, 1957, **79**, 4802; (b) Summerbell and Berger, *ibid.*, 1959, **81**, 633, and references therein.
[4] Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (b) Ch. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, 3rd edn., Vol. I, 2459; (c) Le Fèvre, *Proc. Roy. Soc. New South Wales*, 1961, **95**, 1; (d) Le Fèvre, Sundaram, and Pierens, *J.*, 1963, 479.
[5] Le Fèvre and Sundaram, *J.*, 1962, 1494.
[6] Altona, Romers, and Havinga, *Tetrahedron Letters*, 1959, No. 10, 16.
[7] Henriquez, *Physica*, 1933, **1**, 41.
[8] Caspi, Wittstruck, and Piatak, *J. Org. Chem.*, 1962, **27**, 3183.

TABLE 1.

Incremental Kerr effects, refractive indexes, dielectric constants and densities for solutions containing weight fraction w_2 of solute in benzene * at 25°.

Solute: *trans*-2,3-dibromo-1,4-dioxan, m. p. 73° (I)

$10^5 w_2$	3683	4523	7769
$10^{11} \Delta B$	−640		−1124
$10^4 \Delta \varepsilon$	606	754	1312
$10^4 \Delta d$	196	240	410
$10^4 \Delta n$	14	17	30

$10^{11}\Delta B$: −533, −640, −1124

whence $\Sigma \Delta B / \Sigma w_2 = -1 \cdot 438 \times 10^{-7}$,
$\Sigma \Delta \varepsilon / \Sigma w_2 = 1 \cdot 6726$, $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 5296$,
$\Sigma \Delta n / \Sigma w_2 = 0 \cdot 0382$ and $\Sigma \Delta n^2 / \Sigma w_2 = 0 \cdot 1146$.

Solute: 2,3-dichloro-1,4-dioxan, m. p. 30° (IIa)

$10^5 w_2$	1332	1842	2212	2559	4020
$10^{11} \Delta B$	Zero throughout				
$10^4 \Delta \varepsilon$	258	357	433	500	804
$10^4 \Delta d$	48	61	76	91	134
$10^4 \Delta n$	Zero throughout				

whence $\Sigma \Delta B / \Sigma w_2 = 0$, $\Sigma \Delta \varepsilon / \Sigma w_2 = 1 \cdot 9657$,
$\Sigma \Delta d / \Sigma w_2 = 0 \cdot 3502$, $\Sigma \Delta n / \Sigma w_2 = 0$,
and $\Sigma \Delta n^2 / \Sigma w_2 = 0$.

Solute: 2,3-dichloro-1,4-dioxan, m. p. 52° (IIb)

$10^5 w_2$	336	578	932	1215
$10^{11} \Delta B$	249	426	695	899
$10^4 \Delta \varepsilon$	215	371	600	783
$1 \mathrm{P}^4 \Delta d$	13	22	35	48
$10^4 \Delta n$	6	10	16	20

whence $\Sigma \Delta B / \Sigma w_2 = 7 \cdot 413 \times 10^{-7}$,
$\Sigma \Delta \varepsilon / \Sigma w_2 = 6 \cdot 433$, $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 3855$,
$\Sigma \Delta n / \Sigma w_2 = 0 \cdot 0170$, and $\Sigma \Delta n^2 / \Sigma w_2 = 0 \cdot 0510$.

Solute: 2,3-diphenyl-1,4-dioxen, m. p. 89° (III)

$10^5 w_2$	811	1572	2190	2273	2452	2796	3460
$10^{11} \Delta B$	—	74	91	132	125	—	—
$10^4 \Delta \varepsilon$	64	125	—	175	—	231	274
$10^4 \Delta d$	19	37	—	54	—	65	80
$10^4 \Delta n$	7	15	—	21	—	26	32

whence $\Sigma \Delta B / \Sigma w_2 = 0 \cdot 497 \times 10^{-7}$;
$\Sigma \Delta \varepsilon / \Sigma w_2 = 0 \cdot 7964$; $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 2337$;
$\Sigma \Delta n / \Sigma w_2 = 0 \cdot 0926$; and $\Sigma \Delta n^2 / \Sigma w_2 = 0 \cdot 2778$.

Solute: 2,3-diphenyl-1,4-dioxan, m. p. 46° (IVa)

$10^5 w_2$	1025	1417	1979
$10^{11} \Delta B$	Indistinguishable from zero †		
$10^4 \Delta \varepsilon$	38	48	65
$10^4 \Delta d$	23	32	46
$10^4 \Delta n$	7	10	13

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 0 \cdot 3416$; $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 2285$;
$\Sigma \Delta n / \Sigma w_2 = 0 \cdot 0679$ and $\Sigma \Delta n^2 / \Sigma w_2 = 0 \cdot 2307$.

Solute: 2,3,-diphenyl-1,4-dioxan, m. p. 132° (IVb)

$10^5 w_2$	964	1151	1568
$10^{11} \Delta B$	Indistinguishable from zero †		
$10^4 \Delta \varepsilon$	43	54	67
$10^4 \Delta d$	21	25	34
$10^4 \Delta n$	6	8	10

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 0 \cdot 4453$, $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 2172$,
$\Sigma \Delta n / \Sigma w_2 = 0 \cdot 0652$ and $\Sigma n^2 / \Sigma w_2 = 0 \cdot 1956$.

Solute: " *trans* "-*p*-dioxino[2,3-*b*]-*p*-dioxin, m. p. 134° (V)

$10^5 w_2$	1917	3280	4681
$10^{11} \Delta B$	Indistinguishable from zero †		
$10^4 \Delta \varepsilon$	75	129	182
$10^4 \Delta d$	56	97	138
$10^4 \Delta n$	−3	−5	−8

whence $\Sigma \Delta \varepsilon / \Sigma w_2 = 0 \cdot 3908$, $\Sigma \Delta d / \Sigma w_2 = 0 \cdot 2946$,
$\Sigma \Delta n / \Sigma w_2 = -0 \cdot 0162$, and $\Sigma \Delta n^2 / \Sigma w_2 = -0 \cdot 0486$.

* When $w_2 = 0$, $B_1 = 0 \cdot 410 \times 10^{-7}$, $\varepsilon_1 = 2 \cdot 2725$, $d_1 = 0 \cdot 8738$ and $n_1 = 1 \cdot 4973$. † Owing to the smallness of the Kerr effects and the low solubilities of these compounds, ΔB values could not be measured with certainty.

TABLE 2.

Polarisations, molar Kerr constants, dipole moments, etc., calculated from Table 1.

| Solute	$\alpha \varepsilon_1$	β	γ	δ	$10^{13} {}_\infty ({}_m K_2)$	${}_T P$(c.c.)	R_D(c.c.)	μ * (D)
trans-2,3-Dibromo-1,4-dioxan (I)	$1 \cdot 672_6$	$0 \cdot 6061$	$0 \cdot 025_4$	$-3 \cdot 507$	$-72 \cdot 5$	$110 \cdot 4$	$37 \cdot 8$	$1 \cdot 86$
2,3-Dichloro-1,4-dioxan, m. p. 30° (IIa)								
m. p. 52° (IIb)	$1 \cdot 965_7$	$0 \cdot 4008$	0	0	$-3 \cdot 81$	$90 \cdot 12$	$31 \cdot 5$	$1 \cdot 67$
	$6 \cdot 433_5$	$0 \cdot 4412$	$0 \cdot 011_4$	$18 \cdot 080_5$	$185 \cdot 5$	$219 \cdot 9$	$30 \cdot 9$	$3 \cdot 03$
2,3-Diphenyl-1,4-dioxen (III)	$0 \cdot 7964$	$0 \cdot 2675$	$0 \cdot 061_8$	$1 \cdot 212$	$27 \cdot 1$	$95 \cdot 18$	$71 \cdot 1$	$1 \cdot 00$
2,3-Diphenyl-1,4-dioxan, m. p. 46° (IVa)	$0 \cdot 341_6$	$0 \cdot 2615$	$0 \cdot 045_4$	—	—	$75 \cdot 92$	$68 \cdot 8$	$0 \cdot 42$
m. p. 132° (IVb)	$0 \cdot 445_3$	$0 \cdot 2486$	$0 \cdot 043_6$	—	—	$81 \cdot 66$	$69 \cdot 5$	$0 \cdot 65$
trans-*p*-Dioxino[2,3-*b*]-*p*-dioxin (V)	$0 \cdot 390_8$	$0 \cdot 3371$	$0 \cdot 010_8$	—	—	$43 \cdot 77$	$31 \cdot 2$	$0 \cdot 74$

* Calculated assuming ${}_D P = 1 \cdot 05 \, R_D$.

that the 1,3-interactions between the axial hydrogen and halogen atoms force the rings to deviate from ideal chairs and settle into conformations similar to (A) in solution.

The proposed distortion, expected to be slightly greater for (I) than (IIa), is reflected in the decreasing μ_obs and the increasing ${}_\infty ({}_m K_2)$ obs. in going from (I) to (IIa).

On the other hand, the conformational similarity between (I) and (IIa) as solutes is

shown by the close resemblance of the A_2B_2 splitting pattern in the n.m.r. spectrum of (I), reproduced here as Fig. (1), to that of compound (IIa).[8]

where X = halogen

(A)
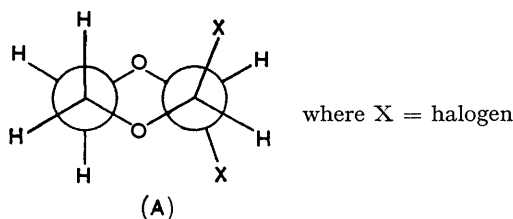
The isomer of 2,3-dichloro-1,4-dioxan (IIb) melting at 52° was assumed to be *cis* *a priori*, because (IIa) is *trans*; and the isomer of 2,3-diphenyl-1,4-dioxan (IVa) melting at 46°, as it was prepared by a Grignard reaction in high yield, was designated *trans* by Summerbell and his co-workers.[3]

TABLE 3.

Previously assigned configurations.

Compound	M. p.	Geometric isomer	Molecular conformation*	Rigidity of the ring
trans-2,3-Dibromo-1,4-dioxan (I)	73	*trans-* [6]	*Caa* [6, 8]	Rigid [6, 8]
2,3-Dichloro-1,4-dioxan (IIa)	30	*trans-* [3a]	*Caa* [6, 8]	Rigid [6, 8]
,, (IIb)	54	*cis-* [3a]	*Bee* [8]	Rigid [8]
2,3-Diphenyl-1,4-dioxan (IVa)	46	*trans-* [3b]	*Caa* ⇌ *Cee* [8]	Flexible [8]
,, (IVb)	132	*cis-* [3b]	*Baa* [8]	Rigid [8]

* Where C =   B =

As early as 1953, melting-point evidence led Stumpf [9] to favour the assignment of a *trans*-configuration to the isomer of 2,3-diphenyl-1,4-dioxan melting at 132° (IVb) and *cis*

c. sec. 400   350   300   250   200

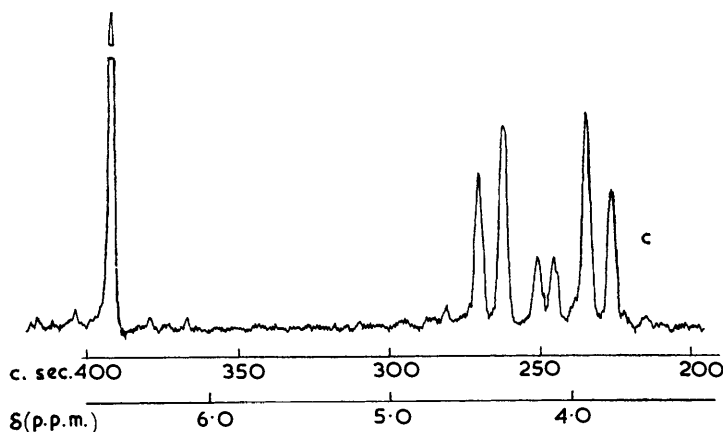δ(p.p.m.)   6·0   5·0   4·0

FIG. 1.   The n.m.r. spectrum of " *trans* "-2,3-dibromo-1,4-dioxan as a solute in deuteriochloroform.

to (IVa).   Nevertheless, after studying the hydrogenation of 2,3-diphenyl-1,4-dioxen (III) (giving the isomers of 2,3-diphenyl-1,4-dioxan (IVa) and (IVb)), Summerbell *et al.*[3b] concluded that ". . . Since catalytic hydrogenation is known to give predominantly the *cis*

.[9] Stumpf, *Z. Elektrochem.*, 1953, **57**, 690.

isomer, the ' *cis* '-configuration in the 2,3-diphenyl-*p*-dioxan series must be assigned to the isomer melting at 136°, and not to the 48° isomer as previously suggested. The 48° isomer must correspondingly be ' *trans* '- ".

Molecular Conformation of 2 3-Dichloro-1 4-dioxan M. p. 52° (IIb), *and the Two Isomeric 2 3-Diphenyl-1 4-dioxans*, M. p. 46° (IVa); M. p. 132° (IVb).— From the geometric assignments shown in Table 3, Caspi *et al.*,[8] after studying the n.m.r. spectra of the compounds mentioned above, conferred molecular conformations *Bee* to (IIb), *Caa* ⇌ *Cee* to (IVa), and *Baa* to (IVb). However, *Bee* cannot be the favoured conformation for (IIb). A conformation such as (B) involves 3 pairs of eclipsed H–H interactions, one eclipsed Cl–Cl dipole interaction, and one 1,4-interaction of the oxygen atoms across the ring. Besides, a boat form of six-membered rings would be much more flexible than a chair, as can be seen from a model, and it is difficult to understand why a conformation such as (B) should be rigid, since the " flipping " of the ring could greatly reduce the strain due to all these interactions. Furthermore, if (IIb) indeed exists as form *Bee* or (B), its dipole moment should not be smaller than 4D, while the experimentally determined moment is only 3D. It cannot be in form *Baa* either, as such a conformation should give a moment of less than 2D.

Finally, the n.m.r. spectrum [8] rules out the possibility that compound (IIb) may exist in form *Cae* or *Bae*, as these conformations require an AB splitting pattern for the 2,3-protons instead of the single peak observed. Therefore, none of the conformations compatible with a *cis* assignment can be assigned to (IIb), and it also must be a *trans*-isomer. Because the other isomer (IIa) has already been proved to be *trans* with the ring in a chair form and the substituents diaxial, the isomer of 2,3-dichloro-1,4-dioxan melting at 54° (IIb) must be in form *Cee*, *i.e.*, with the ring in a chair form and the substituents diequatorial.

The theoretical moment calculated for form *Cee*, if we assume $\mu_{C \cdot Cl} = 1 \cdot 84$ D, is 3·04 D (indistinguishable from that observed) and the $_{\infty}(_{m}K_{2})$'s calculated for this form range from 193×10^{-12} (with b^{C-Cl}'s from methyl chloride) to 256×10^{-12} (with b^{C-Cl}'s from t-butyl chloride); the calculations are summarised in Table 4.

The lower of these values for $_{m}K$ approaches the experimental value of 186×10^{-12}. The assignment of conformation *Cee* to compound (IIb) is thus reconcilable with dipole moment and molar Kerr constants. The nearness of the observed $_{\infty}(_{m}K_{2})$ to that calculated by using bond polarisabilities obtained from methyl chloride, indicates that the dipole–dipole interaction of the two C–Cl links may excercise some " restraint " on the bonding electrons, making them less polarised and less polarisable.

Further support comes from the n.m.r. spectrum of compound (IIb). Its $A_{2}B_{2}$ pattern differs little, if at all, from that of *trans-p*-dioxino[2,3-*b*]-*p*-dioxin (V). As we know that the equatorial substituent will not have any appreciable effect on the protons across the ring, and that the conformation of the dioxinodioxin as two *trans*-fused chairs has never been questioned, the spectral similarity, again, indicates that the two chlorines in compound (IIb) are most probably diequatorial.

For 2,3-diphenyl-1,4-dioxan, m. p. 132° (IVa), a measured moment of 0·65 D excludes the possibility that the ring might have a boat form (which would exhibit a moment of not less than 1·5 D, if μ_{C-Ph} is 0·4 D). Since the molecule is rigid, and only a single, unsplit peak is observed for the C_{2}, C_{3} protons in its n.m.r. spectra,[8] the isomer must be the *trans*-form, contrary to the previous assignment.[3b] It is generally accepted that catalytic hydrogenation gives predominantly the *cis*-isomer;[10] the hydrogenation of 2,3-diphenyl-1,4-dioxen (III) seems to be the first major exception to this rule.

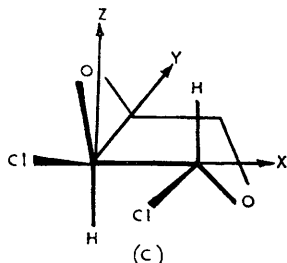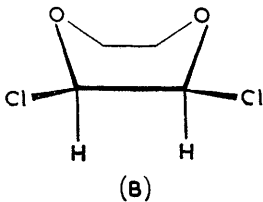[10] Burwell, jun., *Chem. Rev.*, 1957, **57**, 895.

TABLE 4.

Polarisability semi-axes, moment components, etc., for 2,3-dichloro-1,4-dioxan (IIb),
m. p. 54°.

Principal semi-axes *	Direction cosines with †			Dipole moment components, D	$10^{12}{}_{m}K$ calc.
	X	Y	Z		
Calc. with b^{C-Cl}'s from methyl chloride:					
$b_1 = 1.273$	$+0.9125$	0	-0.4091	0	
$b_2 = 1.307$	0	1	0	3.04	$+193$
$b_3 = 1.118$	$+0.4091$	0	$+0.9125$	0	
Calc. with b^{C-Cl}'s from t-butyl-chloride:					
$b_1 = 1.167$	$+0.9497$	0	-0.3131	0	
$b_2 = 1.369$	0	1	0	3.04	$+256$
$b_3 = 1.076$	$+0.3131$	0	$+0.9497$	0	

* Bond polarisabilities used throughout this work are those given in refs. 4c and, for C–O bonds, 4d.   † Where X, Y, and Z are defined as shown in (C).

Now, having concluded that the ring in the isomer, m. p. 132°, of 2,3-diphenyl-1,4-dioxan (IVb) must be in a chair form, with the phenyl substituents *trans*, we can see that the molecular conformation must, therefore, be either *Caa* or *Cee*.   Dipole moment and Kerr effect measurements can offer little help in deciding which of the two is to be favoured, because it is impossible to differentiate between non-polar *Caa* and *Cee* experimentally. However, the n.m.r. spectrum of compound (IVb) does provide some important information in this respect; the portion of the spectrum corresponding to the absorption of the aromatic protons is reproduced as Fig. 2.

The complexity of the spectrum (which does not vary from 35° to 100°) indicates that rotation of the phenyl groups is severely hindered.[11]   In the same spectrum, the series of A_2B_2 peaks centred at $\tau = 6.14$ p.p.m.[8] for the protons at positions 5 and 6 is very similar to those of compounds (IIb) and (V), showing no abnormal shielding of the axial protons by the phenyl rings.   All these facts leave no doubt that the correct conformation for (IVb) must be *Cee* and, because of " overcrowding " in the molecule, the two phenyl rings have to be parallel to each other as illustrated in (D):
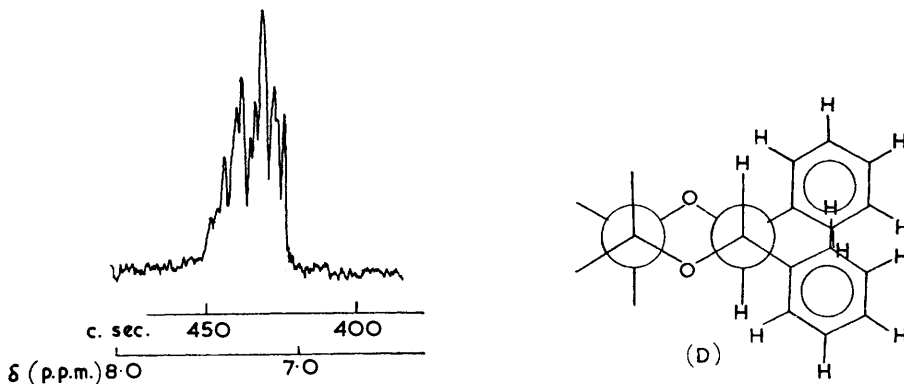

FIG. 2.   The aromatic portion of the n.m.r. spectrum of 2,3-diphenyl-1,4-dioxan, m. p. 132° (IVb).

As for the isomer of 2,3-diphenyl-1,4-dioxan melting at 46° (IVa). a chair form for the dioxan ring is revealed by its small dipole moment of 0·42 D.   Such a finding, in conjunction with the flexibility of the ring, definitely proves that this isomer cannot be *trans* (because if it were *trans* and inverting, it must invert between *Caa* and *Cee*, yet the latter

[11] Curtin, Gruen, Hendrickson, and Knipmeyer, *J. Amer. Chem. Soc.*, 1961, **83**, 4838.

corresponds to the rigid, stable isomer melting at 132°). Therefore, compound (IVa) must be the *cis*-form, as pointed out by Stumpf.[9] Its molecular conformation is best described as inverting between two identical chairs—*Cae* (E) ⇌ (F).


(E)   (F)
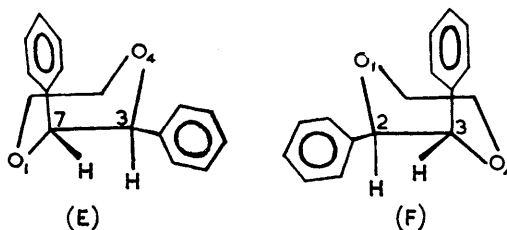
Incidentally, the two peaks in the n.m.r. spectrum of compound (IVa), as recorded here, differ in positions with respect to those given in ref. 8. According to our pre-calibrated spectrum, the lower-field peak occurs at $\tau = 5\cdot50$—$5\cdot60$ and the higher at $\tau = 5\cdot95$—$6\cdot10$ p.p.m. for solutions of concentrations from 3—20%. The shifting up-field of the 2,3-protons compared with those of compound (IVb) does not require any explanation other than that, in compound (IVa), the 2,3-protons while in the equatorial disposition are shielded by the neighbouring phenyl group and " drag up " the average signal between axial and equatorial extremes.

Molecular Conformation of 2,3-*Diphenyl*-1,4-*dioxen* (III).—From its similarity to cyclo-hexene, the dioxen ring would be expected to exist as a " half-chair." [12,13] Following the vector analytical approach of Corey and Sneen,[14] and adopting the following bond lengths —C–C = 1·54, C–O = 1·42, and C=C = 1·34 Å, we see that the molecular geometry of the " half-chair " and the extreme boat forms of the dioxen ring emerge as (G) and (H).

" *Half-chair* "

(G)
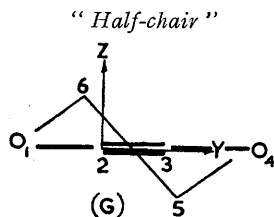
Partial molecular co-ordinates: O_1 ($-0\cdot773$, $1\cdot191$, 0), C_2 (0, 0, 0), C_3 ($1\cdot340$, 0, 0), O_4 ($2\cdot113$, $1\cdot191$, 0), C_5 ($1\cdot333$, $2\cdot308$, $-0\cdot390$) and C_6 ($0\cdot007$, $2\cdot308$, $0\cdot390$).
Ring angles: $\angle O_1 = \angle O_4 = 111°$ 08', $\angle C_2 = \angle C_3 = 123°$ and $\angle C_5 = \angle C_6 = 109°$ 30'.

Extreme boat

(H)
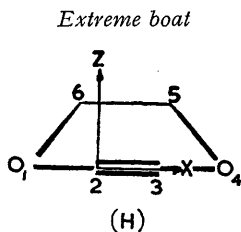
Partial molecular co-ordinates: O_1 ($-0\cdot623$, $1\cdot276$, 0), C_2 (0, 0, 0), C_3 ($1\cdot340$, 0, 0), O_4 ($1\cdot963$, $1\cdot276$, 0), C_5 ($1\cdot440$, $2\cdot058$, $1\cdot064$) and C_6 ($-0\cdot100$, $2\cdot058$, $1\cdot064$).
Ring angles: $\angle O_1 = \angle O_4 = 109°$ 28', $\angle C_2 = \angle C_3 = 116°$ and $\angle C_5 = \angle C_6 = 111°$ 37'.

If $\mu_{C-O} = 1\cdot38$ D, the theoretical dipole moment calculated for a " half-chair " is 0·14 D, while that of the extreme boat is 2·22 D. Therefore, in contrast to the case of cyclohexene, dipole-moment measurements should be able to give information about the nature of the dioxen ring. Dioxen, itself seemingly too unstable, has not yet had its moment measured. For its 2,3-diphenyl derivative (III) we now find $\mu = 1\cdot0$ D, which is between the maximum calculated for the " half-chair " form (J) and the minimum calculated for the boat form (K), these values being 0·54 and 2·22 D, respectively, which are deduced by assuming a value of 0·4 D for μ_{PhC}. Further, the n.m.r. spectrum of the dioxen (III) shows only two single

    [12] Beckett, Freeman, and Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 4227.
    [13] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21; see also Raphael and Stenlake, *ibid.*, 1953, 1286; Orloff, *Chem. Rev.*, 1954, **54**, 409.
    [14] Corey and Sneen, *J. Amer. Chem. Soc.*, 1955, **77**, 2505.

peaks, one at $\tau = 5.66$ (arising from 5,6-protons) and the other at $\tau = 2.80$ p.p.m. (due to the phenyl rings); thus the dioxen ring is indicated as flexible at room temperatures. Since the observed polarity exceeds that expected for (J) or for flatter versions of (J), some participation of (K) may be presumed. On the basis of the moments quoted, 16%

(J)   (K)
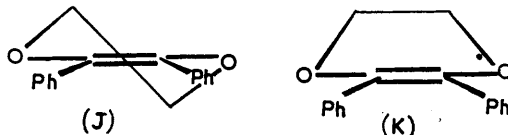
of (K) and 84% of (J) is required to give an apparent moment of 1 D. The contribution from (K) could be even less (down to 1—5%) were a ΔF of ~ 2 k.cal./mole to be assigned between (J) and (K); this appears not unreasonable when compared with the corresponding figure (ΔF 2·7 k.cal./mole), for cyclohexene.[12]

Therefore, we conclude from our dipole-moment measurements that the dioxen ring in 2,3-diphenyl-1,4-dioxene (III) must exist predominantly in a " half-chair " form.

A priori calculations of the theoretical molar Kerr constants cannot be made with certainty owing to lack of definite information about directions of $\mu_{resultant}$, exaltations, etc.; nevertheless, it is qualitatively obvious that the observed $_\infty(_mK_2)$ (27×10^{-12}) is not incompatible with the description given above.