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CONFORMATION OF NON-AROMATIC RING COMPOUNDS—XLIV[1]

NMR SPECTRA AND DIPOLE MOMENTS OF SOME 2-SUBSTITUTED 1,3-DIOXOLANES

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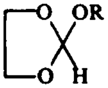
Abstract—Proton spin coupling constants and chemical shifts (AA'BB' part) in a number of 2-substituted 1,3-dioxolanes of the types:



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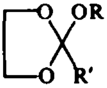

are reported.

Combination of NMR and dipole moment data indicates rotation about the C2—OR bond giving rise to an equilibrium between *anti* and *gauche* forms; the equilibrium constant depends on the bulk of group R.

The mean phase angle of pseudorotation shifts slightly towards that of an envelope form, i.e. towards a smaller torsional angle of the CH_2—CH_2 fragment, on passing from *anti* to *gauche*. From earlier X-ray data on bis-1,3-dioxolane[13] it is deduced that the maximum possible value of φ in 1,3-dioxolanes is about 30°; the actual value in the solid is 21°.

INTRODUCTION

IN PREVIOUS papers the conformation of some 5-membered ring compounds was studied: *trans*-1,2-dihalogenocyclopentanes,[2] 1,1,2-trihalogenocyclopentanes,[3] ring D in steroids[4,5] and halogeno-substituted tetrahydrofuranes.[6] Several physical techniques—X-ray analyses, NMR, IR and Raman spectra and measurements of dipole moments—were combined to yield a consistent picture of the conformational properties. In particular, the exploitation of the linear relationship between vicinal coupling constants and the squares of the dipole moments has proved fruitful.[2,3,7] We now report on this approach in a study of the little-known 2-alkoxy-1,3-dioxolanes, for which compounds a convenient synthetic route has been described.[8]

The stereochemistry and conformation of 1,3-dioxolanes have received considerable attention in recent years,[9–12] but most of the work has been limited to the study of NMR spectra. It is well established that the presence of two different substituents on C2 gives rise to an AA'BB' spectrum of the protons on C4 and C5 (Fig. 1).

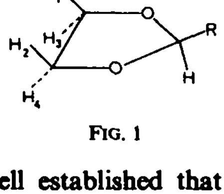

FIG. 1

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It has been stated[9] that the chemical shift of the *cis* hydrogens (H_1 and H_2) of 2-substituted 1,3-dioxolanes depends on the nature of group R; for R = alkyl or aryl the *trans* hydrogens are hardly affected. The present study shows that for R = alkoxy not only the shifts of the *cis* but also those of the *trans* hydrogens are influenced by the nature of R in a complicated manner. Conformational isomerism about the *exo* C2—O bond and pseudorotation of the dioxolane ring seem to play a role.

Three different spin couplings are obtained from the AA'BB' pattern:[9]

$$J_{12} = J_{34} = J_{cis}\ \text{(positive)}$$
$$J_{14} = J_{23} = J_{trans}\ \text{(positive)}$$
$$J_{13} = J_{24} = J_{gem}\ \text{(negative)}$$

The ring is non-planar and the equality $J_{14} = J_{23}$ originates from a rapid interconversion of two equally populated families of pseudorotation conformers (Fig. 2).

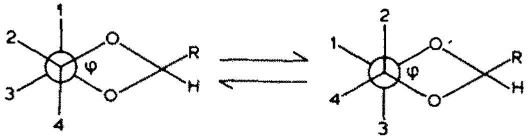
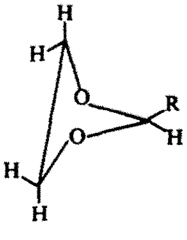


FIG. 2

Each form of Fig. 2 represents the average of a range of conformations of practically equal energy (pseudolibration[2]). No direct information is available about the important average torsional angle of the fragment O—CH_2—CH_2—O of 1,3-dioxolanes in solution. A minimum energy form (half-chair, C_2) with $\varphi \approx 40°$ has been assumed.[9]



Surprisingly, however, consideration of the only published X-ray analysis of a 1,3-dioxolane derivative, bis-1,3-dioxolane,[13] indicates that the CH_2CH_2 fragment is not maximally puckered and, if it were, it cannot attain a torsion angle larger than about 30°.

From the reported atomic parameters of bis-1,3-dioxolane we find the following torsional angles φ (Fig. 3 and Table 1).

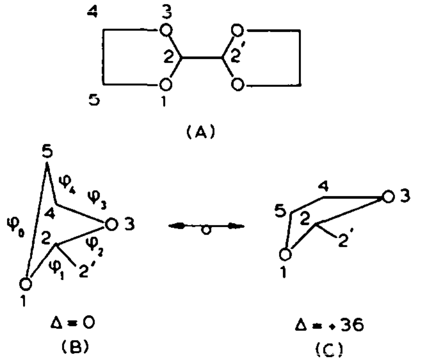


FIG. 3

TABLE 1. OBSERVED TORSIONAL ANGLES IN SOLID BIS-1,3-DIOXOLANE AND CALCULATED ANGLES FOR THE SYMMETRICAL CONFORMATIONS (SEE FIG. 3 AND TEXT).

	calc. C_2 ($\Delta = 0°$)	obs. ($\Delta = +19·1°$)	calc. C_s ($\Delta = 36°$)
$\varphi_0\ (\varphi_5 - 1)$	+30·3°	+30·3°	+29·1°
$\varphi_1\ (\varphi_1 - 2)$	−24·8	−27·9	−29·1
$\varphi_2\ (\varphi_2 - 3)$	+ 9·5	+13·6	+18·0
$\varphi_3\ (\varphi_3 - 4)$	+ 9·5	+ 4·6	0
$\varphi_4\ (\varphi_4 - 5)$	−24·8	−20·7	−18·0

The true geometry of the ring is difficult to depict but it may be considered as being mid-way between the halfchair (C_2) form B and the envelope (C_s) form C. In the solid the *exo* bonds of both rings are (pseudo) equatorial and *anti*.

A more exact definition of the ring conformation is obtained by means of the relation between any torsional angle φ_j in a regula cyclopentane ring and the phase angle of pseudorotation:[4b, 5]

$$\varphi_j = \varphi_m \cos(\tfrac{1}{2}\Delta + j\delta) \tag{1}$$

where $j = 1, 2, 3, 4$; $\delta = 144°$ and φ_m the maximum possible torsional angle. Given two or more torsional angles φ_j, the values of φ_m and can be calculated from Eq. (1). We find $\Delta = 19·1°$ and $\varphi_m = 30·3°$, i.e. the conformation is indeed halfway between C_2 ($\Delta = 0°$) and C_s ($\Delta = 36°$) symmetry. It is easily verified that permutation of the experimental φ_j's in Eq. (1) yields a constant ($\pm 2°$) value of $\Delta - j \times 72°$, as required by theory;[5] the approximation involved (regular bond lengths) does therefore not introduce serious errors.

By substitution of $\Delta = 0°$ and $\Delta = 36°$ in Eq. (1) ($\varphi_m = 30·3°$), we obtain the torsional angles of the symmetrical forms that are part of the same pseudorotation circuit[5] (Table 1).

In the case of 5-membered rings it is *a priori* uncertain whether or not the torsional angles of the molecule as found in the crystal lattice will change to a significant extent on passing into solution. Of course, in solution a complicated mixture of forms under rapid equilibrium may occur, a: with respect to the position on the ring, pseudo axial and pseudo equatorial and b: with respect to the rotation about the *exo* C2—OR bond: *anti* and *gauche* (below). Assuming that the ring geometry is mainly determined by *intra*molecular forces, the true energy minimum along the pseudorotation circuit of the equatorial anti form will correspond more or less closely to the conformation of the ring in the solid. Theoretical justification of this hypothesis rests on consideration of the two strongly conflicting demands made on the ring in solution as well as in the solid:

(a) The tendency to increase the torsional angle of the CH_2CH_2 fragment at the cost of the CH_2—O fragments; the former has undoubtedly the greater energy barrier to internal rotation.

(b) For stereoelectronic and electrostatic reasons the above tendency is opposed by the outspoken preference[14,15] of the O—C—O—C fragments to assume a clinal conformation with $\varphi = 60°$.

The resulting compromise is a form in which φ CH_2—CH_2 $= \varphi 4 = 21°$, equal to the average φ C—O—C—O $= (\varphi_1 + \varphi_2)/2 = 21°$.

On the other hand, the present NMR results (below) indicate that φ_4, and hence the geometry of the entire 5-membered ring, slightly depends upon the conformation about the C2—OR bond. Summarizing, the "best" model of the 1,3-dioxolane ring geometry in solution seems to be one in which the important torsional angle φ (CH_2CH_2) adopts some value in the range 18–25°; the maximum possible value of this angle on further pseudorotation is 30°, i.e. rather smaller than that estimated from observed coupling constants.[11,16]

Dipole moments

The dipole moments of several 2-alkoxy-1,3-dioxolanes and of bis-1,3-dioxolane were determined to detect possible conformational isomerism about the *exo* bond (Table 2).

TABLE 2. DIPOLE MOMENTS (D) IN CARBON TETRACHLORIDE (T) AND IN BENZENE (B) AT 25° OF SOME 1,3-DIOXOLANES

No.	R_1	R_2	μ_T	μ_B
1	OMe	H	1·87	1·81
11	OMe	Me	2·05	2·05
3	OtBu	H	1·41	1·53
4	dioxolane	H	2·06[b]	—

[a] Compound numbers correspond to those in Table 5.

[b] Ref. 17 reported $\mu = 1{\cdot}92$ D in benzene.

Let us first consider the possible conformations of bis-1,3-dioxolane (4).

(i) Assuming a ring geometry such as shown in Fig. 3, two conformations may occur with regard to the possition of group R: pseudo equatorial (e) and pseudo axial (a). Therefore, ring inversion leads to three possible combinations of the two rings: ee, ea and aa.

(ii) Internal rotation about the exo (C2—$C2^1$) bond gives rise to one *anti* and two equal energy *gauche* forms for each of the above named conformations (Fig. 4).

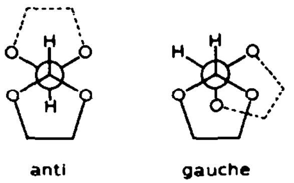


FIG. 4 *Anti* and *gauche* forms of bis-1,3-dioxolane.

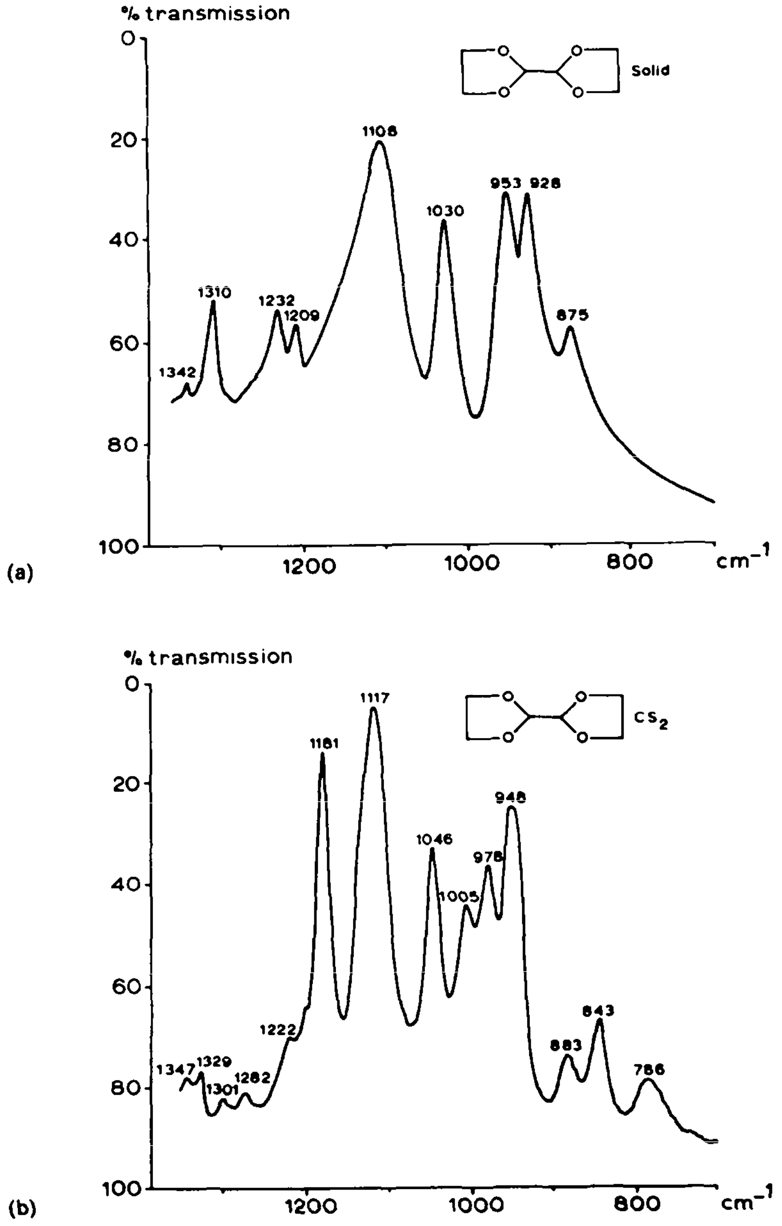


FIG. 5 Infrared spectra of bis-1,3-dioxolane
(a) in the solid (KBr disc)
(b) in carbon disulphide

Theoretically, 6 forms of different energy are possible. In the solid, only one is realized, the *anti*—ee conformation having a center of symmetry and a practically zero dipole moment. Interestingly, the large moment of the compound in solution (2·06 D, compare the moment of 1,3-dioxolane,[18] 1·47 D) indicates a strong predominance of one or more of the polar forms: *gauche*—ee, —ea, —aa or *anti*—ea. Model studies (Cenco Petersen) reveal the presence of several unfavourable short atomic distances in the ea and aa series not occurring in the *gauche*—ee conformation. It seems likely, then, that the latter form predominantes. A dipole moment of 2·1–2·2 D is estimated for this form, in accord with the measured value.

The drastic conformational change of bis-1,3-dioxolane on passing from the solid into solution is also revealed by the IR absorption spectra of the two states. The IR spectrum (Fig. 5) of the solid (KBr disc) bears little resemblance to that of the solution in carbon disulphide. Strong absorption bands of the solid, e.g. those at 928, 1030, 1232 and 1310 cm^{-1}, are not found in the spectrum of the solution, which, moreover, shows many new bands, notably at 786, 843, 978, 1005, 1046 and 1181 cm^{-1}.

The dipole moments of the compounds **1**, **11** and **3** can likewise be understood on the basis of an equilibrium *anti* $\rightleftharpoons$ *gauche*; the equilibrium constant is presumably governed by the balance between steric, stereoelectronic and electrostatic factors (Fig. 6).

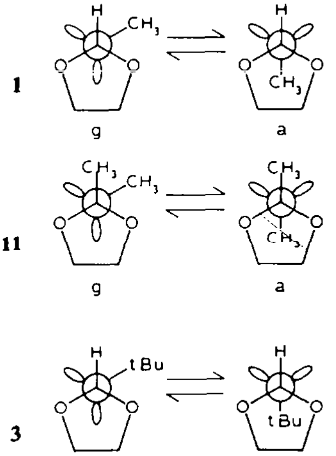


FIG. 6 *Gauche* (g) and *anti* (a) conformers of 2-alkoxy-1,3-dioxolanes.

The *anti* form possesses two clinal C—O—C—O arrangements, thought[14,15] to be more stable than *anti*periplanar C—O—C—O, whereas the *gauche* form contains only one (a similar count explains the preference for the *gauche* conformation in bis-1,3-dioxolane). Hence, notwithstanding greater steric repulsions the *anti* conformer in compound **1** (**1a**) seems to be preferred over **1** g. This tendency, as is witnessed by its larger dipole moment, is strengthened in compound **11** because of the added skew butane interaction. Finally, the tBu group evidently suffers from large steric strain when in anti position and prefers to occupy more or less exclusively the less hindered conformation **3a**, with a low dipole moment. The conformational problems are, of course, more complex than can be dealt with at present since each g and a isomer may occur as an equilibrium mixture pseudo equatorial $\rightleftharpoons$ pseudo axial. Dipole moment studies alone do not provide a clue to a detailed description of these complex systems.

NMR spectra

The AA'BB' patterns recorded are similar to those described in the literature.[9–12] An example is shown in Fig. 7.

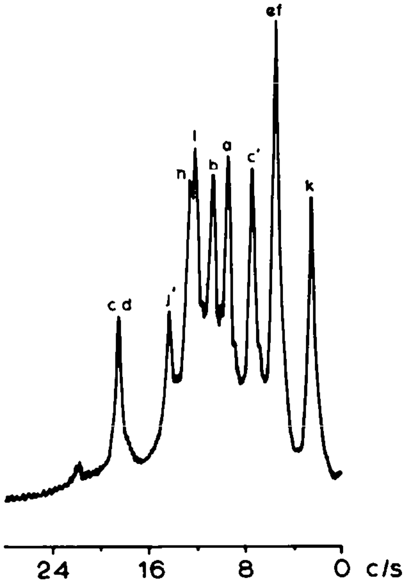


FIG. 7 AA' part of the NMR spectrum (100 Mc) of bis-1,3-dioxolane (4) in $CDCl_3$ ($c' = i$).

The assignment of the peaks follows the notation of Dischler *et al.*[19] The spectral parameters were easily calculated by hand and, in several cases, verified by the use of a computer program.* A further check on the correctness of the assignments was obtained by running the spectra of the majority of the compounds at 2 frequencies (60 and 100 Mc) in various solvents. The coupling constants measured from the 60 and 100 Mc series agreed satisfactorily, the deviations being of the order of 0·05–0·1 c/s. Spectral data[9] for a large number of 2-alkyl-1,3-dioxolanes already indicated narrow ranges of the coupling constants:

	Ref. 9	this work
J_{cis}	6·94–7·52 c/s	6·47–7·27 c/s
J_{trans}	5·94–6·20 c/s	5·88–6·46 c/s
J_{gem}	—7·26– – 7·80 c/s	—7·23– – 7·80 c/s

Our values for J_{trans} and J_{gem} agree well with those of Alderweireldt and Antheunis,[9]

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* We are indebted to Mr. R. Kaptein for the ALGOL version of the Frequint IV program. The calculations were carried out on the X1 computer of this university.

but the range for J_{cis} (the coupling most sensitive to changes in molecular geometry) is extended down to 6·5 c/s. We will return in the discussion to this important point. The gem spin couplings have been discussed[9] and will not be surveyed here.

Table 3 lists the coupling constants and $\nu_0\delta$ values for compounds **1–16**.

TABLE 3. SPECTRAL DATA FOR THE A_2B_2 1,3-DIOXOLANE SYSTEM AT 100 Mc

R_1	R_2	State[a]	J_{cis}	J_{trans}	$-J_{gem}$	$J_{trans} + \frac{1}{2} J_{cis}$	$\nu_0\delta$ (c/s)[b]
1 OMe	H	B	6·80	6·28	7·60	9·68	13·0
		D	—	6·25	7·68	—	11·1*
		T	6·70	6·11	7·31	9·46	10·6
		N	6·80	6·24	7·50	9·64	10·4
2 OEt	H	B	—	6·26	7·52	—	14·5*
		D	—	6·27	7·47	—	12·3
		N	6·8	6·15	7·47	9·57	11·6
3 OtBu	H	B	7·01	6·18	7·29	9·68	20·6
		D	6·98	6·17	—	9·66	18·9*
		T	7·06	6·33	7·35	9·86	17·9
		N	7·05	6·18	7·23	9·71	16·9
4 dioxolane	H	B	6·60	6·13	7·35	9·43	20·1
		D	6·56	6·09	7·67	9·37	10·8
5 OAc	H	B	7·15	6·43	7·64	10·00	12·3
		D	—	6·46	7·64	—	8·3*
6 OPh	H	B	—	6·33	7·52	—	22·5*
		D	6·69	6·30	7·60	9·65	17·3*
		N	6·76	6·15	7·45	9·53	18·4*
7 CCl_3	H	B	6·85	6·27	7·69	9·70	28·7
		D	6·89	6·30	7·70	9·75	20·6
		T	6·86	6·42	7·75	9·86	20·2*
8 SPh	H	B	7·26	6·42	7·80	10·05	23·8*
		D	7·22	6·37	7·66	9·98	20·1*
		N	7·27	6·26	7·68	9·90	21·0*
9 H	H	N	7·3[c]	6·0[c]	—	—	0
10 CH_2Br	H	B	6·61	6·08	7·68	9·38	13·7
		D	6·58	6·02	7·68	9·31	10·4
11 OMe	Me	B	6·56	6·19	7·61	9·47	11·2
		D	—	6·20	7·58	—	10·6*
		T	6·50	6·02	7·30	7·27	9·4
		N	6·62	6·11	7·51	7·42	10·0
12 OEt	Me	B	6·70	6·22	7·64	7·57	13·4
		D	6·70	6·15	7·58	7·50	10·5
		N	6·70	6·15	7·59	7·50	10·0

TABLE 3—*continued*

R_1	R_2	State[a]	J_{cis}	J_{trans}	$-J_{gem}$	$J_{trans} + \frac{1}{2} J_{cis}$	$\nu_0\delta$(c/s)[b]
13 OMe	C_6H_5	B	7·11	6·16	7·44	9·72	17·1
		D	7·13	6·06	7·54	9·63	18·3
		N	7·08	6·09	7·56	9·63	15·9
14 OEt	C_6H_5	B	7·11	6·26	7·58	9·82	19·8
		N	7·12	6·15	7·50	9·71	17·5
15 CHOHPh	C_6H_5	D	6·85	5·88	7·47	9·31	21·0
16 CHOHPhpCl	$p\mathrm{ClC_6H_4}$	B	6·48	6·31	7·95	9·60	16·9

[a] B = benzene, D = deuterochloroform, T = carbon tetrachloride, N = neat liquid.

[b] 100 Mc, $\nu_0\delta$ values indicated by * were calculated from 60 Mc spectra only.

[c] N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* A, **252**, 506 (1959).

DISCUSSION

Having established that the conformation about the C—OR bond depends on the nature of the substituent we may now ask whether the ring geometry is similarly affected. If so, is it possible to construct a consistent model that explains the observed changes in coupling constants and chemical shifts on substitution?

We utilize the previously developed[2,7] linear correlations between various physical properties of a given conformational equilibrium mixture.

The measured properties P, Q and R of an equilibrium mixture of two forms are equated to the properties Pa, Pg, Qa, etc., of the individual conformers by:

$$\begin{aligned} P &= X_g P_g + (1 - X_g) Pa \\ Q &= X_g Q_g + (1 - X_g) Qa \\ R &= X_g R_g + (1 - X_g) Ra \end{aligned} \tag{2}$$

where X_g is the molar fraction of component g.

It follows that: $dP/dQ = (Pg - Pa)/(Qg - Qa) = \Delta P/\Delta Q =$ constant; similarly $dP/dR =$ constant, etc.

On the condition that the individual properties Pg, Pa, ..., are independent of the external influences applied to vary the equilibrium constant, a shift of the equilibrium yields linear relations between the measured properties. Moreover, if we choose properties Pg, Pa, ..., that are constant from compound to compound, a single straight line is obtained for a homologous series of compounds.*

For example, the dipole moments of the individual *anti* and *gauche* forms of 2-alkoxy-1,3-dioxolanes are expected to be practically independent of the nature of the alkoxy group† and a plot of μ^2 vs any other property (coupling constant or chemical shift) permits one to draw several conclusions regarding this second property.

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* In the case of a three-conformer system the relation between two properties, say μ^2 and J, is more complex. Generally, the points will be scattered within the boundary of a triangle (cf. ref. 7 and H. R. Buys, forthcoming thesis, Leiden).

† The dipole moments of homologous series of ethers and alcohols are known to be practically constant; A. L. McClellan, Tables of Experimental Dipole Moments, Freeman and Co., San Francisco (Calif.), 1963).

The experimental results (Fig. 8) indicate that there exists a linear relation between μ^2 and J_{cis} within the error of measurement. First, it follows that the variation of J_{cis} from compound to compound is due to variations in equilibrium composition, J_{cis} (*anti*) being significantly smaller than J_{cis} (*gauche*). Second, the properties of the conformers partaking in the equilibrium, in particular *cis* (*anti*) and J_{cis} (*gauche*), seem to be constant for the a and g conformers of the compounds **1**–**3** in benzene

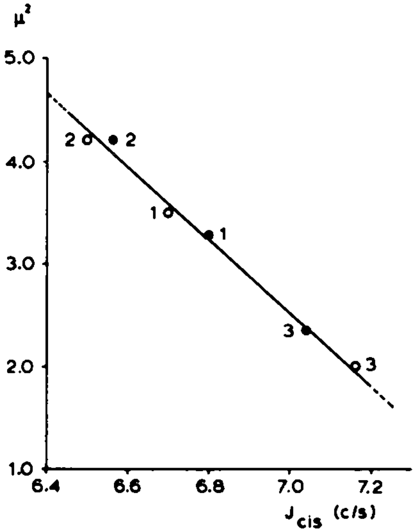

FIG. 8 Plot of μ^2 vs J_{cis} (compounds 1, 3 and 11 in benzene ●) and in carbon tetrachloride ○).

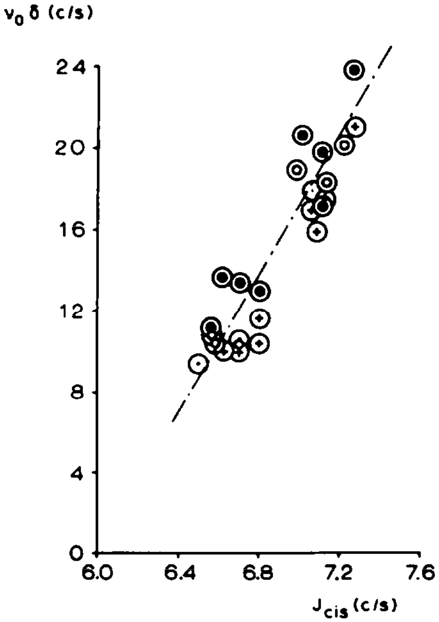

FIG. 9 Plot of $v_0\delta$ vs J_{cis} of 2-substituted 1,3-dioxolanes.
⊙ in benzene, ⊙ in deuterochloroform, ○ in carbon tetrachloride, ⊕ neat liquid.

and in carbon tetrachloride and this is assumed to hold for the remaining compounds also. Third, the occurrence of a single straight line suggests* that two out of the four possible conformers (axial *anti*, axial *gauche*, equatorial *anti*, equatorial *gauche*) predominate in the equilibrium. The available data do not allow an unambiguous choice between a and e conformers.

The chemical shift between the A and B hydrogens ($\nu_0\delta$) is also a physical property expected to vary with the equilibrium *anti* ⇌ *gauche* according to Eq. 2. However, due to substituent-dependent influences on the chemical shift, such as magnetic anisotropy and dipolar effects as well as specific solvent interactions, the correlation between $\nu_0\delta$ and J_{cis} (Fig. 9) or μ^2 shows greater deviations from linearity than the μ^2/J_{cis} plot. Still, the general trend seems clear: increasing J_{cis} (= increasing amount of the *gauche* form) goes with increasing $\nu_0\delta$. Compound 7 (R = CCl_3) shows an anomalously high $\nu_0\delta$ value in benzene; in carbon tetrachloride its shift appears normal.

It was assumed[9] that the signal due to the hydrogens *cis* to the (carbon) substituent on C(2) is shifted upfield. An inspection of the chemical shifts δ_A and δ_B of the 2-alkoxy-1,3-dioxolanes (Fig. 10) leads to the same tentative conclusion, although

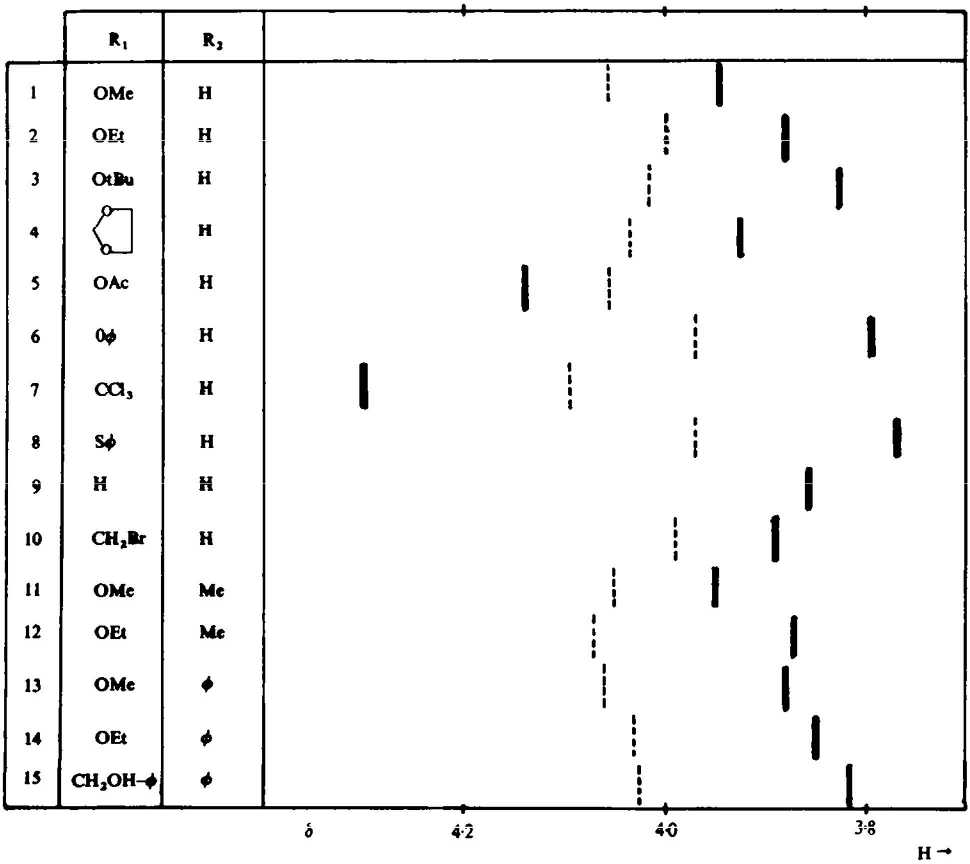

FIG. 10 Chemical shifts (δ in ppm) of the A and B protons of 1,3-dioxolanes in deuterochloroform.

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* See footnote * on page 4385.

matters here are more complicated. In all cases the average shift δ_{AB} is to lower field compared to that of 1,3-dioxolane. Moreover, the downfield resonances in the series R = OMe, OEt, OtBu, Oϕ, Sϕ, occur in a narrow range (3·97–4·06 ppm in $CDCl_3$) whereas the upfield signal progresses fairly regularly from 3·95 to 3·77 ppm, i.e. the *cis* proton signals are shifted progressively upfield, with increasing proportion of the gauche conformers.* This shift may indicate a relatively large contribution from the dipole field of the lone pair electrons on the *exo* oxygen atom.

Coupling constants

The *Karplus* equation[21] is utilized in the following form:

$$J = A\cos^2\varphi_{HH} - B\cos\varphi_{HH} + C \tag{3}$$

$$(0 \leqslant \varphi \leqslant 180°)$$

The theoretical constants,[21] adjusted to Eq. (3), are: $A = 9$, $B = 0{\cdot}5$, $C = -0{\cdot}3$ c/s. These constants are usually treated as empirically adjustable parameters with special emphasis on the largest constant A. Introduction of the ring torsional angle φ (CH_2CH_2) gives:†

$$J_{cis} = J_{\varphi} \tag{4}$$

$$J_{trans} = \tfrac{1}{2}\,[J(120 + \varphi) + J(120 - \varphi)] \tag{5}$$

Eq. (5) takes this form because the ring is inverting rapidly. From Eqs. (3), (4) and (5) we obtain a useful expression:

$$J_{trans} + \tfrac{1}{2}J_{cis} = \tfrac{3}{4}A + \tfrac{3}{2}C \tag{6}$$

Eq. (6) gives a means to check the validity of a general method[11] to determine the

TABLE 4. $J_{trans} + \frac{1}{2}J_{cis}$ (c/s) FOR VARIOUS XCRHCRHY FRAGMENTS

Fragment	Compound	$J_{trans} + \frac{1}{2}J_{cis}$	Ref.
H—CH_2CH_2—H	theor. constants	6·3	21
O—$CHCH_2$—O	carbon subst. 1,4-dioxanes	7·4	14
O—CH_2CH_2—O	1,4-dioxanes	7·9	14
N—CH_2CH_2—O	morpholine	8·1	14
S—CH_2CH_2—O	thioxane	8·7	14
S—CH_2CH_2—S	dithiane	9·4	14
C—CH_2CH—O	cyclohexanols	9·3	[a]
O—CH_2CH_2—O	1,3-dioxolanes	9·71 ± 0·09	[b]
		9·66 ± 0·18	this work

[a] Average value from a number of compounds in the cyclohexane and steroid series.

[b] Average value from the data given in Ref. 9.

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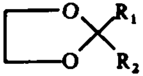
* Excluding 5 and 7; the downfield signal of these compounds is possibly due to the *cis*-protons.

† Trigonal projection symmetry is assumed. Calculations show that the error so introduced is of the order of 2–3°. In view of the more serious approximations involved in the use of a single set of constants in Eq. (3) (the assumption that the electronegative ring oxygen atoms influence the couplings of the a and e protons to an equal extent), it can safely be neglected.

TABLE 5. SOME PHYSICAL CONSTANTS OF THE 1,3-DIOXOLANE DERIVATIVES STUDIED

	R_1	R_2	b.p. °C/mm	b.p. lit.	δH_2 ppm in C_6H_6	δH_{AB} ppm in C_6H_6	δH_{AB} ppm in $CDCl_3$	synthetical procedure	Remarks
1	H	OMe	129–130	128·5^{22}	5·66	3·81	4·00		
2	H	OEt	145–146	145·5^{22}	5·75	3·82	3·94	22	
3	H	OtBu	58–59/13		5·94	3·72	3·92	8	
4	H	dioxolane			5·02	3·56	3·98	19	s.p. 109–111° (109–112°^{19})
5*	H	OAc	41–43/0·5		6·94	3·88	4·10	8	n_D^{20} = 1·4238
6*	H	Oϕ	73–74/0·2		6·20	3·66	3·88	8	
7	H	CCl_3	88–89/14	85–86/12^{23}	5·14	3·64	4·20	23	s.p. 41–42° (41–42°^{23})
8*	H	Sϕ	106–108/0·15		6·66	3·83	3·87	8	
9	H	H	75–76	76	4·75	3·48	3·86		
10	H	CH_2Br	65–66/13	78/24^{9}	4·93	3·60	3·94	9	
11	CH_3	OMe	131–132	132–134^{23}	—	3·85	4·00	8	n_D^{20} = 1·4084 (1·4060^{23})
12	CH_3	OEt	40–41/10	144–145^{23}	—	3·76	3·97	8	n_D^{20} = 1·4109 (1·4079^{23})
13*	ϕ	OMe	128–129/13		—	3·76	3·97	8	n_D^{20} = 1·5112
14	ϕ	OEt	136–137/14	121–126/12^{24}	—	3·74	3·94	8	n_D^{20} = 1,5055
15	ϕ	CHOH—ϕ			—	3·32	3·92	25	s.p. 138–140° (138°^{25})
16*	pClϕ	CHOH—ϕpCl			—	3·25	—	25	s.p. 122–122·5°.

* New compounds.

constants A, B and C for a given X—CH_2—CH_2—Y fragment: this is to regard any change in the couplings of the same fragment in different molecules as due to the change in torsional angle. In that case, $J_{trans} + \frac{1}{2} J_{cis}$ should be constant for each fragment. A compilation of coupling constant data from the literature and from our work (Table 4) reveals that $J_{trans} + \frac{1}{2} J_{cis}$ not only varies with the nature of X and Y, as expected, but also with ring size and/or ring strain. Hence, an attempt to estimate the torsional angle of the CH_2CH_2 fragment in 1,3-dioxolanes from the measured couplings may lead to erroneous conclusions.

The shift of J_{cis} with the *anti* ⇌ *gauche* equilibrium deserves closer attention. Assuming that this shift is mainly due to a change in the average value of φ_4 (Fig. 3 and Table 1), we may conclude that the *mean phase angle of pseudorotation Δ is different for the* anti *and* gauche *forms*, φ gauche < anti. Hence, the *gauche* conformation about the *exocyclic* bond influences in such a way that it tends, on the average, more towards the C_s form (Fig. 3) than the *anti* conformation. The effect is small, however. Let us consider the theoretical change in J_{cis} and J_{trans} on passing from the C_s ($\varphi = 18°$) to the C_2 ($\varphi = 25°$) form. Using Eqs (4) and (5), and taking $A = 9$, $B = 0{\cdot}5$, one finds:

$$J_{cis}(18°) - J_{cis}(25°) = 0{\cdot}084\,A - 0{\cdot}045\,B \simeq 0{\cdot}75 \text{ c/s}$$

$$J_{trans}(18°) - J_{trans}(25°) = -0{\cdot}047\,A + 0{\cdot}060\,B \simeq -0{\cdot}4 \text{ c/s.}$$

Qualitatively, the observed change in J_{cis} on passing from the tBu compound **3** (predominantly *gauche*) to the OMe, Me compound **11** (predominantly *anti*), i.e. 7·3–6·5 c/s, agrees with the calculated change, suggesting that the order of magnitude of the accompanying pseudorotation is about correct. As far as we are aware, this is the first experimental demonstration of the effect of the conformation about the exocyclic bond on the conformation of the 5-membered ring. A similar effect of the nature of the substituent directly attached to ring D of steroids has been reported.[5]

TABLE 6. NUMERICAL DATA OF THE DIELECTRIC MEASUREMENTS

Compound	solvent[a]	α'	β'	P_{20} (cm^3)	R_D (cm^3) (calc)
1	T	4·13	0·19	94·78	23·40
	B	4·27	−0·33	90·68	23·40
11	T	4·99	0·25	114·34	28·02 (R_D exp = 28·07)
	B	5·43	−0·29	113·63	28·02
3	T	2·64	0·36	78·07	37·26
	B	2·80	−0·26	84·91	37·26
4	T	4·99	0·24	119·1	32·08

[a] T = carbon tetrachloride, B = benzene.

EXPERIMENTAL

Syntheses. Details of the synthetical procedures and analyses of the products will be given elsewhere.[8] B.ps, refractive indices and chemical shifts are collected in Table 5.

Dielectric measurements. The electric moments were determined by measuring dielectric constants and densities of 4–6 solutions of the compound in CCl_4 and in benzene (molar fraction range 0–0·025) at 25°

as described.[2,7] The total polarization P_{20} was calculated by the method of Halverstadt and Kumler;[26] dipole moments followed from:

$$\mu = 0{\cdot}01281 \times 10^{-18} [(P_{20} - R_D) T]^{\frac{1}{2}}$$

NMR spectra. The 60 Mc spectra were taken with a Varian A-60, the 100 Mc spectra with a Varian HA-100 NMR spectrometer, using TMS as internal standard. The solutions in benzene, $CDCl_3$ and CCl_4 were approximately 15% wt/vol.

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