39. *The A_2B_2 Proton Resonance Spectrum of 2-Methyl-1,3-dioxolan.*

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The A_2B_2 proton resonance spectrum of the ring protons of 2-methyl-1,3-dioxolan is reported and analysed in detail. It is shown that the $\cos^2 \phi$ law cannot precisely account for the magnitude of the couplings in the dioxolan and dioxan rings. This conclusion is supported by other recent determinations of coupling constants in cyclic compounds.

THE analysis of complex nuclear magnetic resonance (n.m.r.) spectra has been the subject of many investigations. The basic theory was given first by McConnell[1] and Pople.[2] The A_2B_2 system * (in the nomenclature of Pople *et al.*[2]) is one of the most important types of n.m.r. spectrum, and the original analysis [2] has been extended [5-7] and applied to a number of such systems.[8-15]

In the course of an investigation into the conformation of various acetals,[16] it was observed that the ring protons of 2-methyl-1,3-dioxolan (I) gave rise to a complex A_2B_2 p.m.r. spectrum of a type different from any that had previously been investigated. The almost identical spectrum of ethylene sulphite had been reported [17] but no analysis given. In this system the pair of protons on each side of the ring are equivalent. In this respect the system is formally similar to the A_2B_2 spectra of 1,1-disubstituted cyclopropanes.[13,14] However, owing to the very different magnitudes of the coupling constants involved, the observed spectrum is quite different. Also, as there are many weak and degenerate transitions, it is not possible without some knowledge of the assignment of the transitions to

* This system has also been described as the AA'BB' system.[3,4]

[1] McConnell, McLean, and Reilly, *J. Chem. Phys.*, 1955, **23**, 1152.
[2] Pople, Schneider, and Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill, 1959.
[3] Musher, *Mol. Phys.*, 1961, **4**, 311.
[4] Whitman, *J. Mol. Spectroscopy*, 1963, **10**, 250.
[5] Dischler and Englert, *Z. Naturforsch.*, 1961, **16a**, 1180.
[6] Abraham and Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.
[7] Grant and Gutowsky, *J. Chem. Phys.*, 1961, **34**, 699.
[8] Abraham and Bernstein, *Canad. J. Chem.*, 1959, **37**, 2095.
[9] Grant, Hirst, and Gutowsky, *J. Chem. Phys.*, 1963, **38**, 470.
[10] Martin and Dailey, *J. Chem. Phys.*, 1962, **37**, 2594.
[11] Abraham and Pachler, *Mol. Phys.*, 1964, **7**, 165.
[12] Sheppard and Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506.
[13] Hutton and Schaefer, *Canad. J. Chem.*, 1963, **41**, 2429.
[14] Wiberg and Nist, *J. Amer. Chem. Soc.*, 1963, **85**, 2788.
[15] Gutowsky and Juan, *Discus. Faraday Soc.*, 1962, **34**, 52.
[16] Robinson, personal communication.
[17] Pritchard and Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.

obtain the coupling constants uniquely, even with the use of an iterative computational procedure. Thus, the analysis of this system is given in detail.

Analysis of the Spectrum.—The spectrum is conveniently described in terms of the parameters $K(J_A + J_B)$, $M(J_A - J_B)$, $N(J + J')$, and $L(J - J')$,[2] where J, J', etc., are as shown in (I).

The spectrum can be analysed in two ways. First by the use of tables of calculated spectra [18] to obtain an approximate fit. However, inspection of such tables was of no use without an estimate of the probable value of the coupling constants of the compound. As these depend on the conformation of the molecule (see later) only ranges of values can be given, *e.g.*, $J_A \simeq J_B = J_{cis}$ (5—10 c./sec.); [19,20] $J = J_{gem}$ (*ca.* -10 c./sec.) [17,21] and $J' = J_{trans}$ (2—8 c./sec.).[20,21] The nearest set of values in ref. 18 is $J_A = J_B = 4$ c./sec.; $J = -6$ c./sec., $J' = 4$ c./sec., and δ_{AB} 6 c./sec. The calculated spectrum (No. 5—110) only resembles the observed spectrum (Fig. 1) in general outline (owing mainly to the large width of the " calculated " lines), but it is of some use as, *e.g.*, it demonstrates that there could be three unresolved transitions within the largest peak. However, the assignments of the observed transitions (from which all the coupling constants can be obtained explicitly) have still to be found, as these are not given in ref. 18. These can be found from the rules given by Pople [2] and Dischler,[5] *e.g.*, if $M(J_A - J_B)$ is zero or very small (as would be expected) then transitions 9,10 and 11,12 are degenerate. Thus we obtain, by writing (9,10) for the energy of the degenerate pair of transitions, the following rules:

$$
\begin{aligned}
1 - 3 \;\; &= N \\
\left. \begin{array}{l} 1 + 3 \\ 5 + 8 \\ 6 + 7 \end{array} \right\} &= \sqrt{N^2 + \delta^2}
\end{aligned}
\qquad
\begin{aligned}
(9,10) - (11,12) &= L \\
(9,10) + (11,12) &= \sqrt{L^2 + \delta^2} \\
5 - 6 &= 7 - 8
\end{aligned}
\tag{1}
$$

where all the transition energies are measured from the mid-point of the spectrum, *i.e.*, $\frac{1}{2}(\delta_A + \delta_B)$. All the molecular parameters can be found from the above except K. This may be obtained explicitly from the little known rule (due to Dischler [5])

$$K = 2 - 4 + 7 - 8 - N \tag{2}$$

Consideration of the observed transition energies together with eqn. (1) leads to the assignment of the spectrum shown in Fig. 1. The A_2B_2 spectrum is symmetric with respect to the signs of M and L, but is dependent on the relative signs of K and N. Thus, reversal of the assignments of (9,10) and (11,12), *i.e.*, change of the sign of L, will not affect the spectrum at all. However, reversal of the assignments of 1 and 3 (*i.e.*, change of the sign of N) will do so. From eqn. (2) this will give two values for K. The spectrum was computed for both these sets of parameters. The calculated spectrum (shown in Fig. 1) is for N negative, the other calculated spectrum did not agree at all with the observed spectrum and is not given here. Note that transition 8 lies under transitions (11,12) of the other half of the spectrum. The values of N, L, K, and δ found were -1.53, 13.5, 14.2, and 9.9 c./sec., respectively, with M zero. The negative sign of L follows directly from the now well established difference in the relative signs of J_{gem} and J_{vic} in these systems.[21] This gives $J_A = J_B = 7.1$ c./sec., $J = -7.5$ c./sec. and $J' = 6.0$ c./sec.*

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* After this manuscript was submitted, the author's attention was directed to a similar analysis of the 1,3-dioxolan ring in 3-bromo-2-thiophen aldehyde ethyleneacetal.[21a] The analysis of this less well resolved spectrum (only 12 of the 20 possible lines were observed) gave coupling constants identical to those found above but a quite different spectral assignment. There is now agreement [21b] that the assignment in Fig. 1 is the correct assignment on the normal $A_2X_2 \rightarrow A_2B_2$ correlations.[2]

[18] Wiberg and Nist, " The Interpretation of N.M.R. Spectra," W. A. Benjamin, Inc., 1962.
[19] Abraham and McLauchlan, *Mol. Phys.*, 1962, **5**, 195; *ibid.*, p. 513.
[20] Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 747.
[21] Fraser, Lemieux, and Stevens, *J. Amer. Chem. Soc.*, 1961, **83**, 2105.
[21a] Mathiasson, *Acta Chem. Scand.*, 1963, **17**, 2133.
[21b] Mathiasson, personal communication.

K

In the analysis of such unusual spectra, the spectrum is often shown as a function of all the spectral parameters in turn, *e.g.*, in this case δ, N, L, and K. Such spectral correlations serve mainly to provide information from which the assignment of the transitions can be made simply and easily. The coupling constants in the system are usually only affected by changes in the molecule, *e.g.*, changing the C_2 substituent and in this case all the coupling constants will be affected. Thus spectral correlations as a function of one coupling constant are of limited value. However, the chemical shift between the A and B protons may be changed in a number of ways, *e.g.*, by solvent effects, in different magnetic fields, as well as by molecular changes. Thus the spectrum has been calculated for a range of
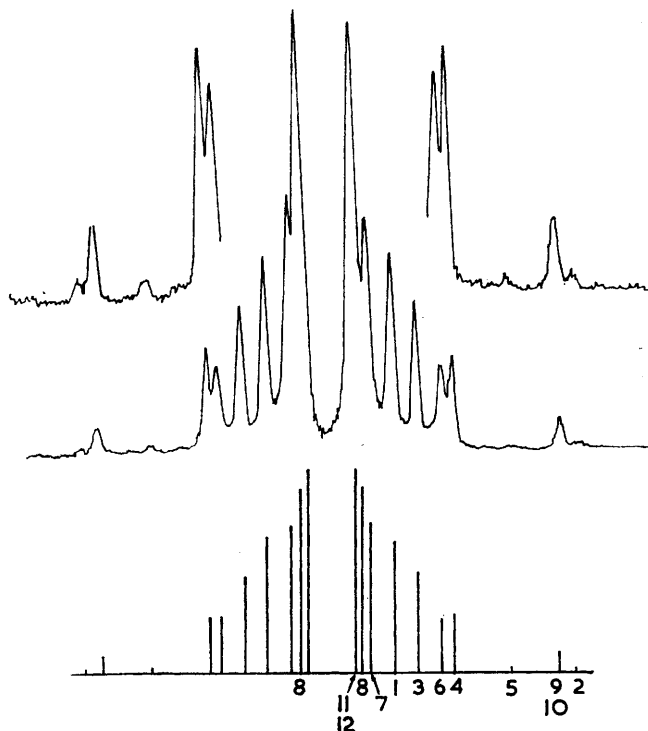
FIG. 1.   The observed and calculated nuclear magnetic resonance spectrum of 2-methyl-1,3-dioxolan (1/1 in benzene) at 60 Mc./sec.

values of the chemical shift difference (Fig. 2). From this the assignments and, therefore, the molecular parameters in any spectrum of this type can easily be obtained. For example, the 40 Mc./sec. p.m.r. spectrum of ethylene sulphite has been reported previously.[17] Inspection of this spectrum (which is very similar to that in Fig. 1) gives immediately the assignment and the following molecular parameters: N —1·9 c./sec., L —14·8 c./sec., K 13·2 c./sec., M zero, and δ 10·7 c./sec. These give $J_A = J_B = 6\cdot6$ c./sec., J —8·4 c./sec., and J' 6·5 c./sec. The 60 Mc./sec. spectrum of (I) in $CDCl_3$ is even less resolved than the spectrum in benzene (Fig. 1), in that transition 6 has now coalesced with 9, 10, and 8. However, from transitions 1 and 3 both N (1·7 c./sec.) and more important δ (8·1 c./sec.) can be obtained. This value of δ gives τ_A 6·02 and τ_B 6·16. From the known deshielding effect of 1,3-diaxial methyl interactions [22] and of the 3-axial methyl on the C_1 proton in six-membered rings [23] we may provisionally assign the low field peaks to the protons *cis* to the C_2 methyl.

[22] Abraham and Holker, *J.*, 1963, 806.
[23] Eliel, Gianni, Williams, and Stothers, *Tetrahedron Letters*, 1962, 735.

The Coupling Constants and Conformations of Dioxan and Dioxolan.—The coupling constants obtained above can be combined with measurements of other similar fragments to test the well known $\cos^2 \phi$ law,[24] which can be written as

$$J = \frac{k_1 \cos^2 \phi \qquad 0° \leqslant \phi \leqslant 90°}{k_2 \cos^2 \phi \qquad 90° \leqslant \phi \leqslant 180°} \qquad (3)$$

where ϕ is the dihedral angle between the relevant C–H bonds and $k_{1,2}$ constants. Both the extensive use of this equation and the known limitations of the valence bond treatment
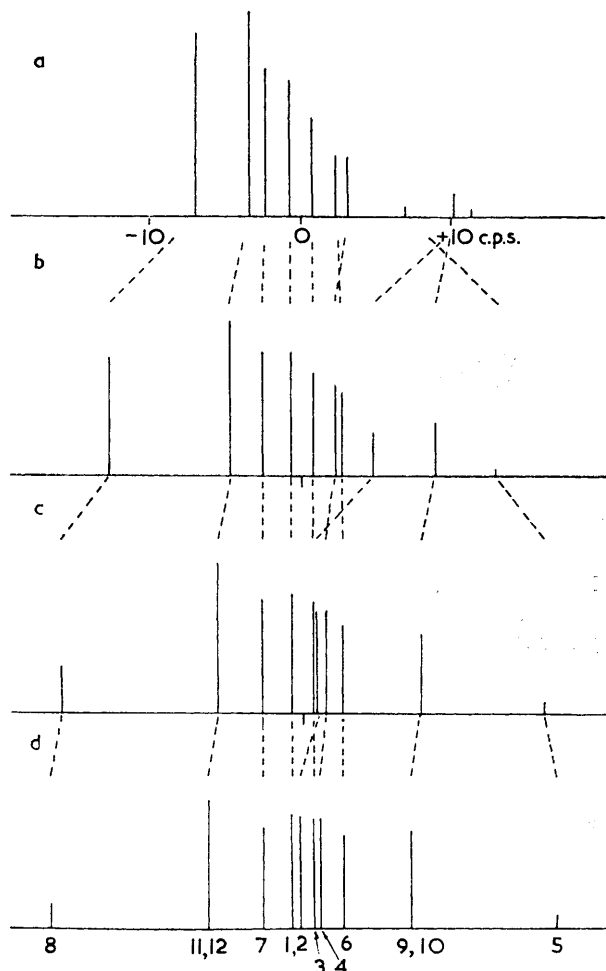
FIG. 2. The calculated spectrum and assignments of the B_2 group of an A_2B_2 spectrum from δ_B with N, L, M, and K —1·53, 13·5, 0, and 14·2 c./sec., respectively, and δ 10 c./sec. (*a*), 20 c./sec. (*b*), 40 c./sec. (*c*), and 100 c./sec. (*d*).

used to obtain it [24] make it essential that the equation be tested experimentally. However, very few attempts have been made to do this. Anet [24a] found good agreement between the observed coupling constants of the rigid camphane-2,3-diols and those predicted using the theoretical values of $k_{1,2}$. It is now clear that the parameters $k_{1,2}$ depend on the substituents attached to the CH·CH fragment and the theoretical values are not in general applicable.[11] Abraham and McLauchlan [19] measured a large number of coupling constants

[24] Karplus, *J. Chem. Phys.*, 1959, **30**, 11; *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[24a] Anet, *Canad. J. Chem.*, 1961, **39**, 789.

in hydroxyproline and allohydroxyproline, from which $k_{1,2}$ and ϕ were determined for each CH·CH$_2$ fragment. The self consistency of the values of ϕ provided a test of eqn. (3). Good agreement was found for hydroxyproline but only fair agreement for the highly strained ring of allohydroxyproline. However this type of approach is very limited in scope.

Here a third more general method is given. This is to measure the coupling constants of the same fragment in different molecules, in which any change in the couplings can be regarded as due merely to the change in the dihedral angle. Consider the O·CH$_2$·CH$_2$·O fragment in dioxan and dioxolan. The values of the *cis* and *trans* coupling constants are 2·7 and 6·1 $\pm$ 0·2 c./sec. in dioxan [12] and 7·3 and 6·0 $\pm$ 0·3 c./sec. in dioxolan.[12,25] The values for 2-methyl-1,3-dioxolan above (7·1 and 6·0 $\pm$ 0·1 c./sec.) are identical within the experimental error with the dioxolan results and confirm the provisional assignment. Assuming 120° dihedral angles between the methylene C–H bonds and one stable ring conformation (plus the mirror image as the rings are inverting rapidly), we can write J_{cis} and J_{trans} as

$$\begin{aligned}
J_{cis} &= J\phi = k_1 \cos^2 \phi \\
&= \tfrac{1}{2}(J_{120+\phi} + J_{120-\phi}) \\
J_{trans} &= \tfrac{1}{2}[k_2 \cos^2 (120+\phi) + k_1 \cos^2 (120-\phi)]
\end{aligned} \qquad (4)$$

where ϕ is the O·C·C·O dihedral angle in the particular ring considered. In this case the dioxan and dioxolan results give two sets of equations like (4) in the four unknowns $k_{1,2}$ and the dihedral angles of the two rings, and can therefore be solved exactly. However, mere inspection of these equations is sufficient to demonstrate their inconsistency; the identical values of J_{trans} in the two rings imply from (4) that the dihedral angles are identical. This, besides its inherent implausibility, is inconsistent with the widely different values of J_{cis}. The best fit is given by using $k_{1,2} = 11·3$ and 11·8 c./sec., respectively, and $\phi = 58°$ for dioxan and 38° for dioxolan. The calculated values of J_{cis} and J_{trans} are 3·1 and 7·2 for dioxan and 7·0 and 5·2 for dioxolan, which agree only to 0·5—1·0 c./sec. with the observed values. These values of $k_{1,2}$ lie between the theoretical values used by Sheppard [12] which agree with the dioxan but not the dioxolan couplings and those of Lemieux [25] who considered only the dioxolan couplings.

In order to relate the above result to the $\cos^2 \phi$ law itself, it is necessary to consider the assumptions made in deriving eqn. (4). A calculation using 125° dihedral angles between the H·C·H· bonds only changed J_{trans} to 6·8 c./sec. in dioxan and 5·4 c./sec. in dioxolan, thus any likely deviation from 120° will not affect the above conclusions. Also, integration of eqn. (4) over a range of dihedral angles was performed for dioxolan, as the ring could be considered, like cyclopentane,[26] to exist in a large number of energetically equal forms. However, this always increases J_{cis} and decreases J_{trans} and thus gives much poorer agreement with the observed couplings. Clearly, although the $\cos^2 \phi$ law with single values of the parameters k_1 and k_2 gives a qualitative description of the observed results, it does not provide a precise explanation of them.

Discussion.—The above conclusions are supported by recent investigations on coupling constants in cyclic compounds. These couplings show a variation which is too large to be explained satisfactorily on the basis of the electronegativity of the substituents and the ring conformations. We will restrict this discussion to CH$_2$·CH$_2$ fragments in molecules which are either planar or flipping rapidly between two mirror image conformations. In both cases eqn. (4) may be used. This equation will obviously predict changes in the couplings as the dihedral angle of the CH$_2$·CH$_2$ fragment changes. If we assume for simplicity $k_{1,2} = 10$ c./sec. then J_{cis} would decrease from 10 to 2·5 c./sec. and J_{trans} increase from 2·5 to 6·3 c./sec. as ϕ changes from 0 to 60°. However, $J_{cis} + J_{trans}$ (which can always be obtained from the spectrum even though the actual values of J_{cis} and J_{trans} cannot always

[25] Lemieux, Stevens, and Fraser, *Canad. J. Chem.*, 1962, **40**, 1955.
[26] Hendrickson, *J. Amer. Chem. Soc.*, 1961, **83**, 4537.

be determined) remains relatively constant decreasing from 12·5 to 8·8 c./sec. The different electronegativities of the substituents on the $CH_2 \cdot CH_2$ fragment will give rise to further variations in the coupling constants. Again, the extreme cases being taken (the $O \cdot CH_2 \cdot CH_2 \cdot O$ and $C \cdot CH_2 \cdot CH_2 \cdot C$ fragments), the equation predicts values of 5·5 and 7·0 c./sec. for the average couplings in the two cases,[11] *i.e.*, a variation of about 20%.

The observed variation in cyclic compounds is much larger than the above considerations would suggest, *e.g.*, in three-membered rings in which conformational differences do not arise J_{cis} and J_{trans} vary from 5·0 and 3·2 c./sec., respectively, in ethylene oxide [12] to 9·7 and 6·9 c./sec. in 1-phenylcyclopropanecarboxylic acid.[13] This is almost twice the predicted variation. The three-membered ring may be considered a special case as the bonding is by no means sp^3; however the same phenomenon occurs in all other ring systems. For example, in four membered rings, in which again variations in conformation will be almost negligible, J_{cis} and J_{trans} are 11·2 and 7·8 c./sec., respectively, in 2,2-dibromocyclobutanone [28] whereas their sum is 15·0 c./sec. in trimethylene oxide [27] and only 12·2 c./sec. in propio-lactone.[2] Similarly in five-membered rings, J_{cis} and J_{trans} are 9·2 and 3·6 c./sec., respectively, in indan-1-one,[29] but 7·3 and 6·0 c./sec. in dioxolan and increase to 10·8 and 8·0 c./sec. in 2-methyl-4,5-dihydrofuran.[30] Although conformational differences will affect the couplings in the five-membered rings, the dihedral angle variation would be expected to be much less than 60°, and thus again the predicted range of values of the couplings much less than is observed. Furthermore, in six-membered rings similar variation occurs although the couplings are generally smaller than in the other rings (as predicted by eqn. 4); in dioxan J_{cis} and J_{trans} are 2·7 and 6·1 c./sec., and $J_{cis} + J_{trans}$ is 9·1, 9·1, 9·4, 10·3, and 13·7 c./sec. in morpholine, dihydropyran, N-methylpiperazine, Δ^3-piperidine,[27] and 4,4-dimethylcyclo-hexanone,[30] respectively. Here again the variation in the dihedral angle would account for only about half the observed variation.

These large variations are all the more remarkable when compared with the relative insensitivity to environmental effects (apart from the $\cos^2 \phi$ dependence) of vicinal couplings in acyclic compounds. The dependence of $CH_3 \cdot CH$ couplings on both the electronegativity of the substituents and the state of hybridisation of the methine carbon atom is relatively small, *e.g.*, the coupling constants of such extreme cases as ethyl-lithium and ethyl fluoride are 8·4 and 6·9 c./sec., respectively,[11] and the $CH_3 \cdot CH$ couplings in propane and propene are very similar in magnitude (7·3 and 6·4 c./sec., respectively,[31,32]).

It is clear that other factors besides the $\cos^2 \phi$ law and the electronegativity of the substituents are affecting the coupling constants in cyclic systems. It is noteworthy that a dependence of the *cis*-olefinic coupling constant on ring size has recently been reported in some cyclic olefins.[33] More significantly the value of the geminal coupling constant in saturated systems changes markedly on cyclisation; the geminal coupling between the C_6 methylene protons in some sugar acetates of *ca.* 12·3 c./sec. changes to *ca.* 8·5 c./sec. in the corresponding 3,6-anhydro-compounds in which the methylene group is part of a five-membered ring.[34] In both geminal [35] and olefinic coupling constants [24] there are mechan-isms affecting the couplings which are not present in vicinal couplings; however the available evidence does seem to point to the possibility that changes in the valence angles in the $CH \cdot CH$ fragment (apart from the dihedral angle) may affect the values of the coupling constants. Obviously more investigations are needed to isolate these other effects.

[27] Varian Associates, N.M.R. Spectra Catalogue, 1962.
[28] Servis and Roberts, *J. Phys. Chem.*, 1963, **67**, 2885.
[29] Lustig, personal communication.
[30] Abraham, unpublished results.
[31] Waugh and Dobbs, *J. Chem. Phys.*, 1959, **31**, 1235.
[32] Bothner-By and Naar-Colin, *J. Amer. Chem. Soc.*, 1961, **83**, 231.
[33] Chapman, *J. Amer. Chem. Soc.*, 1963, **85**, 2014.
[34] Abraham, Hall, Hough, and McLauchlan, *J.*, 1962. 3699.
[35] Barfield and Grant, *J. Chem. Phys.*, 1962, **36**, 855.

EXPERIMENTAL

The spectra were recorded on a Varian A-60 spectrometer, using side band modulation to measure the peak positions. The coupling constants are accurate to better than $\pm 0\cdot1$ c./sec. and τ values to $\pm 0\cdot01$ p.p.m.