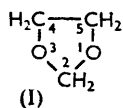


161. *Spectra of Acetals. Part I. The Infrared and Raman Spectra of 1 : 3-Dioxolan.*

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Values have been assigned to 25 of the 27 fundamental vibrational modes of 1 : 3-dioxolan, as indicated in Table 2.

THE infrared spectra of 1 : 3-dioxolan (I), together with a number of substituted dioxolans and acyclic acetals and ketals, have been reported^{1,2} over a limited range (1030—1190 cm.⁻¹) and some assignments suggested. The Raman and infrared spectra (see Figure) of 1 : 3-dioxolan are now reported and assigned. The aim of this research was the eventual application of this knowledge to the interpretation of the spectra of sugar acetals and ketals containing substituted dioxolan ring systems.



The exact geometry of the dioxolan ring is not known although Mills³ suggested that the ring is nearly planar. However, the diffuse nature of the Raman lines and breadth of the infrared bands indicated a puckered ring. In the region 1200—1300 cm.⁻¹, 1 : 3-dioxolan shows a broad band in its Raman spectrum which stretches over *ca.* 70 cm.⁻¹ and

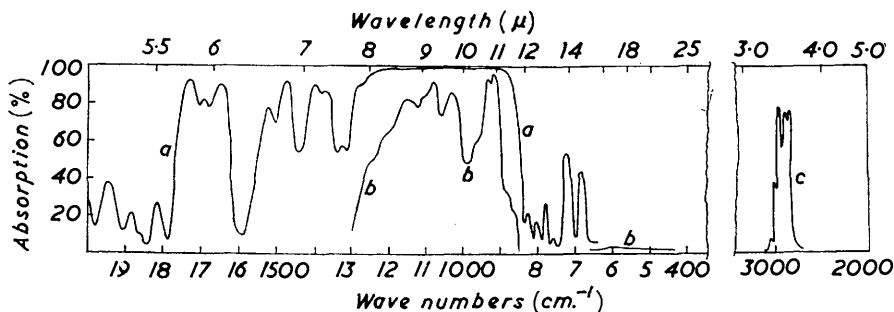
¹ Bergmann and Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

² Lagrange and Mastagli, *Compt. rend.*, 1955, **241**, 1947.

³ Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 13.

is just identifiable as two very broad diffuse lines. The corresponding infrared bands were so broad and ill-defined that the centres were difficult to locate. Similar broad bands were present in the spectra of cyclopentane and tetrahydrofuran, which are known to be

Infrared spectrum of 1:3-dioxolan, b. p. 74–75° (single peak on vapour chromatography, (a) in 0.1 mm. cell, (b) as liquid film, and (c) in CCl₄).



puckered,^{4,5,6} but were absent from the spectrum of 1:3-dioxol-2-one,⁷ which is known to be planar.

EXPERIMENTAL

Purification of 1:3-Dioxolan.—Commercial 1:3-dioxolan (34 ml.) and lead dioxide (3 g.) were heated under reflux for 2 hr., cooled, and filtered. Xylene (40 ml.) and lead dioxide (2 g.) were added to the filtrate and the mixture fractionally distilled. Xylene (20 ml.) and sodium wire (ca. 3 g.) were added to the main fraction, b. p. 70–71°, and, after the vigorous reaction had subsided, the mixture was refractionated and the main fraction, b. p. 73–74°, collected. Sodium wire was added to the product from the first fractionation, and after refractionation the fraction of b. p. 74–75° was collected.

Measurement of Spectra.—The Raman spectra were recorded photographically on a Hilger Raman spectrometer, with a filter solution⁸ containing 4% of *p*-nitrotoluene and 1 part in 12,000 of Rhodamine 6GBN 500 (supplied by Imperial Chemical Industries Limited) which, because of decomposition by the mercury-lamp source, was renewed after every 4 hours' exposure. The filter solution transmitted 86% of the exciting line (4358 Å), the transmission falling off rapidly on either side of this wavelength. The transmission of the strong mercury lines at 4047 and 4078 Å was reduced to <6% and <12%, respectively, and that of a barium impurity at 4554 Å to 58%.

The Raman lines were measured within ± 1 cm.⁻¹ against standard iron-arc lines. Qualitative polarisation data were obtained from exposures with polaroid wrapped around the Raman tube.⁹

The infrared spectra were measured on a Grubb-Parsons single-beam spectrometer with a sodium chloride and a potassium bromide prism. The carbon-hydrogen stretching frequencies were measured in the third order on a grating spectrometer having a 2500 lines/inch grating. Measurements were carried out in the vapour state, in liquid films of 0.02–0.1 mm. thickness, and as solutions (M/3) in carbon tetrachloride.

DISCUSSION

Since the degree of puckering in the dioxolan ring is probably small⁴ the symmetry will not deviate far from that of a planar ring. Application of the selection rules¹⁰ to

⁴ Kilpatrick, Pitzer, and Spitzer, *J. Amer. Chem. Soc.*, 1947, **69**, 2483.

⁵ Miller and Inskip, *J. Chem. Phys.*, 1950, **18**, 1519.

⁶ Le Fèvre and Le Fèvre, *Chem. and Ind.*, 1956, 54.

⁷ Angell, *Trans. Faraday Soc.*, 1956, **52**, 1178.

⁸ Edsall and Wilson, *J. Chem. Phys.*, 1938, **6**, 124.

⁹ Crawford and Horwitz, *ibid.*, 1947, **15**, 268.

¹⁰ Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

such a planar ring (cf. ref. 5) indicates that twenty-seven normal vibrations are expected for 1:3-dioxolan and these are shown, according to the symmetry class to which they belong, in Table 1. The molecule has a two-fold axis (the z axis) and two planes of symmetry, that of the ring (yz) and that through the two-fold axis and perpendicular

TABLE 1. Selection rules for 1:3-dioxolan.

Symmetry class	Total no. of vibrations	Ring vibrations	Hydrogen vibrations	Infra-red	Raman
A_1	9	4	5	M_z	Polarised
A_2	5	1	4	Inactive	Depolarised
B_1	6	1	5	M_x	Depolarised
B_2	7	3	4	M_y	Depolarised

TABLE 2. Assignments (cm.^{-1}) for 1:3-dioxolan.

Activity	Vibration	Assignment (cm.^{-1})	
		Infrared	Raman
<i>Symmetry class A_1</i>			
Infrared parallel z , B band, Raman polarised	Sym. C-H stretch (C_2)	2857s	2852m d PP
	Sym. C-H stretch (C_4 , C_6)	2889s	2894vs b P
	CH_2 scissors (C_2)	1509s	1509s shp
	Sym. CH_2 scissors (C_4 , C_6)	1480s	1481s shp
	Sym. CH_2 wag (C_4 , C_6)	1361s sh	1352w
	Ring stretch	1087vs	1088w m PP
	Ring stretch	1030vs	1038vw
	Ring stretch (breathing)	939vs	939vs shp P
	Ring bend (in-plane)	NI	658vw
<i>Symmetry class A_2</i>			
Infrared inactive, depolarised	Raman Antisym. C-H stretch (C_4 , C_6)	—	2972s bd
	CH_2 twist (C_2)	(1251)w vb	1246m vb
	Antisym. CH_2 twist (C_4 , C_6)	(1208)w vb	1210m vb
	Antisym. CH_2 rock (C_4 , C_6)	—	1009w
	Ring bend (out-of-plane)	—	—
<i>Symmetry class B_1</i>			
Infrared, parallel x , C band, Raman depolarised	Antisym. C-H stretch (C_2)	2998m	—
	Antisym. C-H stretch (C_4 , C_6)	2964s	(2972)s bd
	Sym. CH_2 twist (C_4 , C_6)	1286w sh	—
	CH_2 rock (C_2)	723m	725w—m
	Sym. CH_2 rock (C_4 , C_6)	921vs	—
	Ring bend (out-of-plane)	—	—
<i>Symmetry class B_2</i>			
Infrared, parallel y , A band, Raman depolarised	Sym. C-H stretch (C_4 , C_6)	2889s	2894vs bd
	Antisym. CH_2 scissors (C_4 , C_6)	1480s	1481s shp
	CH_2 wag (C_2)	1397s	1397w—m
	Antisym. CH_2 wag (C_4 , C_6)	1327w	1329w
	Ring stretch	1158vs	—
	Ring stretch	961s sh	962w—m
	Ring bend (in-plane)	680m	671vw

Key: v, very; s, strong; m, medium; w, weak; P, polarised; PP, partially polarised; b, broad; d, diffuse; sh, shoulder; shp, sharp; NI, not investigated.

to the plane of the ring (xz). (These axes are chosen in accordance with the latest recommendations.¹¹) Dioxolan therefore belongs to the point group C_{2v} . The assignments made are in Table 2. (Evidence for certain of the assignments was obtained from the spectra of substituted dioxolans which are given in the following paper.)

Symmetrical C-H Stretching Vibrations.—By analogy with the cyclopentane spectrum these vibrations would be expected near 2870 cm.^{-1} . The absorption (2857 cm.^{-1}) assigned to the symmetrical C-H stretching vibration of the 2-methylene group is also shown by 4-methyldioxolan, but not by any of the 2-substituted dioxolans. The corresponding

¹¹ Report on Notation for the Spectra of Polyatomic Molecules, *J. Chem. Phys.*, 1955, **23**, 1997.

Raman line (2852 cm.^{-1}) was too diffuse to determine whether, as would be predicted, it was polarised. The two symmetrical C-H stretching vibrations of the 4- and the 5-methylene group were allocated to almost the same frequency (infrared 2889 cm.^{-1} ; Raman 2894 cm.^{-1}) as that assigned by Angell⁷ to similar vibrations in dioxol-2-one.

Antisymmetrical C-H Stretching Vibrations.—Although a Raman line corresponding to the infrared band (2998 cm.^{-1}) assigned to the antisymmetrical C-H stretching vibration (B_1) of the 2-methylene group has not been observed, the Raman line at *ca.* 2972 cm.^{-1} is very broad and diffuse and stretches up to *ca.* 2990 cm.^{-1} . A comparison with the substituted dioxolans is not possible for this frequency, as in these compounds it is overlaid by a methyl vibration. To the out-of-phase antisymmetrical C-H stretching vibration (A_2) of the 4- and the 5-methylene group has been assigned the strong diffuse Raman line at 2972 cm.^{-1} , and the strong infrared band at 2964 cm.^{-1} has been assigned to the corresponding in-phase vibration (B_1). The two frequencies are close and the Raman line corresponding to 2964 cm.^{-1} is probably overlaid by the diffuse line at 2972 cm.^{-1} . The assignment of the higher frequency to the out-of-phase vibration is in agreement with Angell's⁷ assignments for dioxol-2-one, although in this case there is a difference in frequency of some 40 cm.^{-1} .

Methylene Scissoring Vibrations.—The frequency (1509 cm.^{-1}) assigned to the scissoring vibration of the 2-methylene group is also displayed by 4-methyldioxolan but not by any 2-substituted dioxolan. The corresponding in-phase (A_1) and out-of-phase (B_2) scissoring vibrations of the 4- and the 5-methylene group have been assigned the same frequency (1480 cm.^{-1}): this coincidence is supported by the decrease in intensity, without alteration in frequency, when one of these groups is substituted. The Raman line at 1480 cm.^{-1} appears depolarised, but this is not unexpected as the polarised A_1 line is overlaid by the depolarised B_2 line. It is of interest that the frequency increases as the methylene group is linked first to one oxygen atom ($-\text{O}-\text{CH}_2-\text{C}-$) and then to two ($-\text{O}-\text{CH}_2-\text{O}-$) (cf. methylene scissoring vibrations in *cyclopentane*, 1455 cm.^{-1} ; in *tetrahydrofuran*, 1450 and 1489 cm.^{-1}).

Methylene Wagging Vibrations.—Here again comparison of previous assignments of methylene wagging modes in *cyclopentane*,⁵ *tetrahydrofuran*,¹² and *dioxol-2-one*⁷ indicate that attachment of a methylene group to an oxygen atom increases its frequency. Hence the wagging vibration frequency of the 2-methylene group has been assigned the value 1397 cm.^{-1} , and the symmetrical (A_1) and antisymmetrical (B_2) wagging vibrations of the 4- and the 5-methylene group the frequencies 1361 and 1327 cm.^{-1} , respectively. All three assignments are supported by the spectra of the substituted dioxolans.

Methylene Twisting Vibrations.—The appearance of a weak infrared band at *ca.* 1251 cm.^{-1} is probably due to the fact that selection rules do not apply strictly in the liquid state since the moderately strong Raman line at *ca.* 1246 cm.^{-1} assigned to the twisting vibration (A_2) of the 2-methylene group is also shown by 4-methyldioxolan but not by 2-methyl- or the 2:4-dimethyl-dioxolans. The other A_2 twisting vibration, the antisymmetrical one involving the 4- and the 5-methylene group, has been assigned to the moderately strong Raman line at *ca.* 1210 cm.^{-1} . The assignment of the weak infrared band at 1286 cm.^{-1} to the corresponding symmetrical vibration (B_1) is less certain because no information was available on the direction of the change of dipole moment. For both the twisting vibrations and the rocking vibrations discussed below, the oxygen atom does not appear to have a recognisable effect on frequencies.

Methylene Rocking Vibrations.—The frequency (723 cm.^{-1}) assigned to the rocking vibration of the 2-methylene group is also displayed by 4-methyldioxolan but not by the 2-substituted dioxolans. The weak Raman line at 1009 cm.^{-1} has been assigned to the antisymmetrical rocking vibrations of the 4- and the 5-methylene group, since there is no corresponding infrared band as required by the symmetry type (A_2). The analogous symmetrical vibration (B_1) has been assigned the frequency of the strong infrared band

¹² Tschamler and Voetter, *Monatsh.*, 1952, **83**, 302.

at 921 cm^{-1} . The corresponding Raman line has not been observed, as is consistent with a rocking vibration.

Ring Vibrations.—Four of the five ring stretching vibrations are readily identified since they give rise to intense infrared lines which are also present in the spectra of the substituted dioxolans. The frequency at 939 cm^{-1} can be unequivocally assigned to the ring breathing vibrations (A_1) since it is the strongest Raman line below 1500 cm^{-1} and is highly polarised. The higher frequency (cf.: tetrahydrofuran, 913 cm^{-1} ; cyclopentane, 886 cm^{-1}) was to be expected on introduction of a further oxygen atom into the ring. The polarisation of the Raman line corresponding to the infrared band at 1087 cm^{-1} indicates that this ring stretching vibration is of the A_1 symmetry class. Although the Raman line at 1038 cm^{-1} was too weak for the polarisation to be ascertained, the corresponding infrared absorption at 1030 cm^{-1} showed a band shape indicating¹³ a dipole moment change parallel to the z axis. This frequency has therefore been assigned to an A_1 vibration. Bergmann and Pinchas¹ also assigned this band to a symmetrical ring stretching vibration.

One of the two remaining ring stretching vibrations, which should be of the B_2 symmetry type, has been assigned to the very strong infrared band at 1158 cm^{-1} , in agreement with Bergmann and Pinchas¹ who assigned this to an antisymmetrical stretching vibration. The other ring stretching vibration is assigned tentatively the value 961 cm^{-1} .

The A_1 in-plane ring deformation has been assigned to the weak Raman line at 658 cm^{-1} . The Raman line is too weak for polarisation data but in the 2:2-dimethyldioxolans the intensity of the corresponding line at 638 cm^{-1} is very much enhanced by coupling of the in-plane ring deformation with the symmetrical stretching vibration of the *gem*-dimethyl group. The corresponding line in 2:2-dimethyl-1:3-dioxolan, which has the same symmetry as 1:3-dioxolan, is strongly polarised. The B_2 in-plane deformation has been assigned the moderately strong infrared band and weak Raman line at *ca.* 680 cm^{-1} . A strong infrared band has been observed near this frequency in some, and a Raman line in all but one, of the substituted dioxolans, confirming the assignment of this frequency to a ring vibration. The two assignments (658 and 680 cm^{-1}) reflect the upward trend of frequency with introduction of oxygen atoms into the ring system (cf. in-plane ring deformation of cyclopentane, 545 and 617 cm^{-1} ; in-plane ring deformations of tetrahydrofuran, 596 and 650 cm^{-1}).

The two fundamentals to which frequencies have not been assigned are the out-of-plane ring frequencies. These almost certainly lie below the limit of infrared measurements (420 cm^{-1}) and have not been observed in the Raman effect. If the out-of-plane puckering can occur at different ring atoms, the interchange co-ordinate between the puckered arrangements accounts for one of the degrees of freedom for the out-of-plane deformation. This motion is not describable by a simple harmonic motion and would need to be treated by special methods, as would the second out-of-plane ring motion, which would depend largely on the atom which was instantaneously out of the plane.

The failure of the infrared spectrum of 1:3-dioxolan vapour to show recognisable band shape, with one exception at 1030 cm^{-1} , has been a serious handicap in the assignment of frequencies. The polarisation of the Raman lines has only been a little more helpful, for of the five polarised lines expected below 1400 cm^{-1} , only one highly polarised line and one partially polarised line have been observed as polarised.

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¹³ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197; Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.