Dimerisation of 2-Phenyl-1,3-dioxan-5-one: X-Ray Crystal Structure of 2,10-Diphenyl-1,3,6,9,11,13-hexaoxadispiro[4.1.5.2]tetradecane

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A cis–trans mixture of 2-phenyl-1,3-dioxan-5-ol has been oxidised with ruthenium tetraoxide to 2-phenyl-1,3-dioxan-5-one which dimerises in carbon tetrachloride solution at room temperature. The dimer is shown by X-ray crystallographic analysis to be racemic 2,10-diphenyl-1,3,6,9,11,13-hexaoxadispiro[4.1.5.2]tetradecane. A mechanism for its formation is proposed.

2-PHENYL-1,3-DIOXAN-5-ONE (2) was required as a model compound for inclusion in a photochemical study of ketones containing alkoxy-substituents.[1] Marei and Raphael [2] prepared this ketone by periodate cleavage of a vicinal amino-alcohol and found that it hydrated readily. They also reported that it could not be prepared by oxidation of the corresponding alcohol (1), presumably with conventional oxidants.

[1] P. M. Collins and P. Gupta, J. Chem. Soc. (C), 1971, 1965.
[2] A. A. Marei and R. A. Raphael, J. Chem. Soc., 1960, 886.

Because of our interest [3,4] in ruthenium tetraoxide we decided to study the oxidation of alcohol (1) with this oxidant, since we have shown that it should be eminently suitable for this purpose; it functions well in the presence
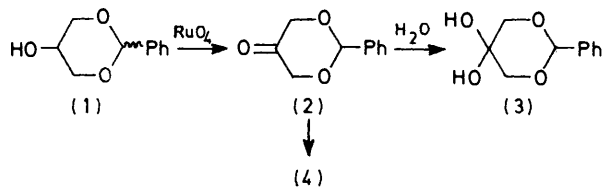
of alkoxy- and related substituents and furthermore hydroxylic solvents are not required at any stage of its reaction; consequently it is ideal for preparing ketones which readily form gem-diols.[3,5]

A solution of cis- and trans-2-phenyl-1,3-dioxan-5-ol (1) in anhydrous carbon tetrachloride was treated in the usual way with ruthenium tetraoxide [3,4] until g.l.c. analysis showed that all the alcohol (1) had reacted. One product was formed, which was assumed to be the required ketone (2), since a filtered portion of the reaction solution gave, upon evaporation, an oil with a ketone carbonyl absorption, $v_{max.}$ 1750 cm^{-1}, and a ^{1}H n.m.r. spectrum in [^{2}H]chloroform which showed a singlet at δ 4·40 due to four methylene protons, a singlet at 5·80 from a benzylidene methine proton, and a multiplet at 3·40 due to five aromatic protons. Treatment of this oil with moist ether gave the known [2] crystalline gem-diol (3). Its ^{1}H n.m.r. spectrum in [^{2}H$_6$]acetone exhibited a broad singlet at δ 2·80 which was exchangeable with deuterium oxide, for two hydroxy-protons, a pair of doublets (δ 4·44 and 4·50, J_{gem} 16 Hz) (each 2H) due to four methylene protons, and the expected signals for the phenyl group and benzylidene proton. The ^{1}H n.m.r. spectrum of a sample of the gem-diol in [^{2}H]-chloroform, however, was identical with that of the parent ketone, and consequently the diol (3) must dehydrate readily and go into solution as the ketone (2) in this solvent, a conclusion corroborated by $v_{max.}$ 1750 cm^{-1} exhibited by the chloroform solution.

The remainder of the reaction solution was evaporated to a low volume in anticipation that ketone (2) would crystallise. A crystalline product did appear after 24 h and increased in amount during one month at 0° to give a 62% yield of compound X with m.p. 138°, which differed from that reported [2] for ketone (2), m.p. 69—71°. The elemental analysis, molecular weight, and ^{1}H n.m.r. spectrum, which exhibited signals for two benzylidene residues and four methylene groups, all showed that compound X was a dimer of ketone (2), and because the i.r. spectrum showed no unsaturation apart from the

phenyl groups, a diphenylated tricyclic structure was assigned to X.

Conceptually the simplest structure for X would be a dimer formed by addition of two ketone carbonyl groups to give either 1,2- or 1,3-dioxetan derivatives. Although the former are known,[6] they are very unstable and are only prepared by indirect means and the latter have only been postulated [7] as transient intermediates, and thus neither is likely. The spectroscopic results do not exclude such compounds, and neither do they permit a detailed structure to be assigned to X. This was achieved by X-ray crystallographic analysis (see below), which showed that dimerisation had occurred with concomitant rearrangement to give 2,10-diphenyl-1,3,6,9,-11,13-hexaoxadispiro[4.1.5.2]tetradecane (4) as a racemate.

Ruthenium derivatives were not involved in the dimerisation, since ketone (2) prepared by the original route [2] also forms the dimer just as readily. The dimer has been formed in several experiments and in some of these moisture was not rigorously excluded. For example, the dimer crystallised from carbon tetrachloride solutions of (2) which were open to the atmosphere, even though such conditions would be expected to produce the gem-diol (3).
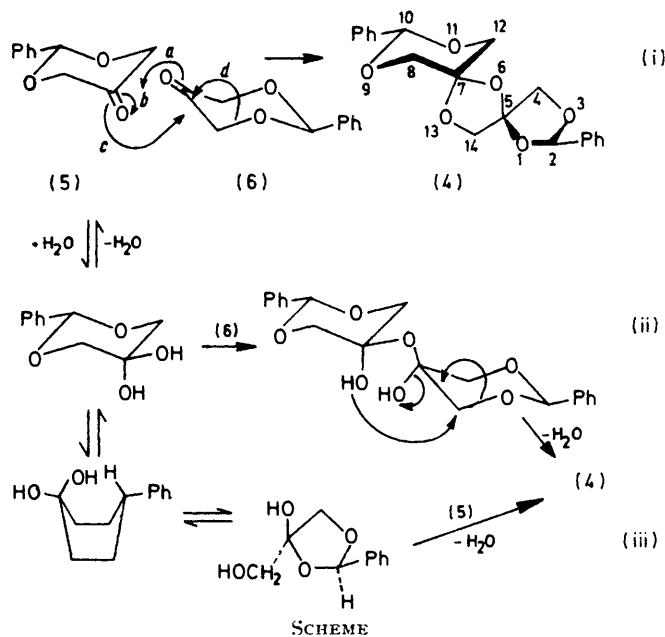
Scheme

Dimer (4) might be formed in several ways. The carbonyl oxygen atom in one molecule could attack the carbonyl carbon atom in another * to give either a zwitterionic intermediate [see arrows a and b in the Scheme (i)], which then ring closes with concomitant re-

* Such nucleophilic additions do occur with aldehydes (e.g. trioxan from formaldehyde), although they are less common with ketones, except for cyclisations of 1,4-diketones to give furan derivatives; however, these reactions usually require catalysts.

[3] P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, J. Chem. Soc. (C), 1966, 1131.

[4] P. J. Beynon, P. M. Collins, D. Gardiner, and W. G. Overend, Carbohydrate Res., 1968, 6, 431; P. M. Collins, P. T. Doganges, A. Kolarikol, and W. G. Overend, ibid., 1969, 11, 199.

[5] P. M. Collins and W. G. Overend, J. Chem. Soc., 1965, 3448.

[6] F. McCapra, Chem. Comm., 1968, 155; K. R. Kopecky and C. Mumford, Canad. J. Chem., 1969, 47, 709; P. D. Bartlett and A. P. Schaap, J. Amer. Chem. Soc., 1970, 92, 3223; S. Mazur and C. S. Foote, ibid., p. 3225.

[7] N. C. Yang, W. Eisenhardt, and J. Libman, J. Amer. Chem. Soc., 1972, 94, 4030.

arrangement (see arrow *d*), or alternatively dimer (4) directly [see arrows *a*, *c*, and *d* in the Scheme (i)]. If water were involved then one hydrated molecule could attack another molecule in the ketonic form as shown in the Scheme (ii). On the other hand the hydrated molecule could rearrange to a dioxolan derivative, and then add to a molecule of the ketone as shown in the Scheme (iii).* These equilibria are displaced to the right by crystallisation of the dimer.

Four diastereoisomers could arise from dimerisations of this type and it is of note that the isomer isolated is that which arises from reaction between the dioxanone derivatives in their most stable chair conformations, in

methylene group; it follows therefore that the doublet at 3·68 and quartet at 3·91 must arise from the C-12 methylene group. The other four doublets (J —9·5) cannot be assigned to specific positions in the dioxolan rings. This analysis of the methylene proton signals is corroborated by the size of geminal coupling constants (^2J). It is known from studies [10] with tetrahydropyran and tetrahydrofuran derivatives that ^2J values for methylene groups adjacent to the ring oxygen atoms (*i.e.* the α-position) are more negative in six-membered rings than in five-membered rings. Consequently the four signals which possess the more negative ^2J coupling (*i.e.* —11·5 Hz) can be assigned to the methylene groups

TABLE 1

^{1}H N.m.r. parameters [chemical shifts (δ); J in Hz] for compound (4) measured at 220 MHz in C_6D_6

H-2	H-10	H8-*eq*	Protons at C-14 and -4		H-12*eq*	H-8*ax*	H-12*ax*	Protons at C-14 and -4		Aromatics	
5·75	5·25	4·36 *	3·98 †	3·90 †	3·91	3·71 *	3·68	3·45 †	3·26 †	7·6	7·2
s	s	q	d	d	q	d	d	d	d	m	m
		^2J —11·5	^2J —9·5	^2J —9·5	^2J —11·5	^2J —11·5	^2J —11·5	^2J —9·5	^2J —9·5		
		^4J 2·8			^4J 2·8						

* Assigned by double resonance studies at 100 MHz. † This partial assignment is made because the intensity pattern of these signals shows that the protons appearing at low field are each coupled to one of the protons appearing at high field.

which the phenyl groups are equatorial as shown in the Scheme (i) and (ii). Formation of the other three diastereoisomers would require at least one of the molecules involved in the dimerisation to adopt a chair conformation in which a phenyl group was axially disposed on the dioxan ring.

With the structure of (4) established it is possible partially to analyse its ^{1}H n.m.r. spectrum. The methylene proton signals can be divided into two groups of four protons each, those which are geminally coupled by —9·5 † and those geminally coupled by —11·5 Hz † (see Table 1). The latter group can be further divided into two protons which appear as doublets, and two which appear as quartets. The protons giving rise to quartets must be long-range-coupled to each other through at least four bonds. The structural element in compound (4) which is most likely to give rise to long range coupling is formed by the atoms H-8*eq* ‡, C-8, -7, and -12, and H-12*eq*.‡ These form a W array which permits effective coupling between H-8*eq* and H-12*eq*.[9] Therefore the quartets (^2J —11·5 and ^4J 2·8 Hz) at δ 4·36 and 3·91 must be due to H-8*eq* and H-12*eq*. The lower field signal of these two probably originates from H-8*eq*, since this proton is in the neighbourhood of four oxygen atoms (O-1, -6, -9, and -13), whereas the other higher field signal at 3·91 is probably due to H-12*eq*, which is reasonable, since it is near only three oxygen atoms (O-6, -11, and -13).

Spin decoupling, carried out at 100 MHz, showed that the doublet at δ 3·71 was coupled to the quartet at 4·36, and consequently these signals must be due to the C-8

which form part of the dioxan ring whereas those with ^2J —9·5 Hz must be part of the dioxolan, which agrees with the assignment made above.

The assignment of the benzylidene protons, as shown in Table 1, is tentative and has been made on the basis of the observation that benzylidene protons in dioxolan rings resonate at lower field than those in dioxan rings.[11]

Description of the Structure.—The crystal structure of 2,10-diphenyl-1,3,6,9,11,13-hexaoxadispiro[4.1.5.2]tetradecane consists of discrete molecules, one of which is shown by a stereodrawing in Figure 1. A schematic drawing of the molecule showing the labelling of the atoms and the intramolecular bond lengths and angles is given in Figure 2 and further details of the molecular geometry are recorded in Table 2.

The environment about the spiro-carbon atom C-5 is distorted. The dioxolan ring angles O-1–C-5–C-4 and O-6–C-5–C-14 are less than the tetrahedral value [the average is 103·5(3)°], which permits the C-14–C-5–C-4 angle to open out to 117·9(2)°. This distortion minimises the non-bonded interactions between the bulky methylene groups at C-4 and C-14 by affording a separation of 2·581(5) Å between C-4 and C-14. This interatomic distance is larger than the distances between O-1 ⋯ C-14, C-4 ⋯ O-6, and O-1 ⋯ O-6 which are 2·421(4), 2·401(4), and 2·306(3) Å respectively.

The environment about the second spiro-carbon atom C-7 is also distorted. The dioxolan ring angle O-6–C-7–O-13 is 106·3(2)°, and this decrease from the tetrahedral

* We thank a referee for suggesting this mechanism.
† It is assumed that both these couplings are negative.
‡ These atoms are represented as H-8 and H-12 in Tables 2(*d*) and 3(*c*).

[8] F. A. Bovey, ' Nuclear Magnetic Resonance Spectroscopy,' Academic Press, New York, 1969, p. 129.
[9] S. Sternhell, *Quart. Rev.*, 1969, **23**, 261.
[10] R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron*, 1966, Suppl. 7, 355.
[11] N. Baggett, K. W. Buck, A. B. Foster, M. H. Randall, and J. M. Webber, *J. Chem. Soc.*, 1965, 3994.

value is compensated for by an increase in the C-12-C-7-O-13 angle to 112·7(3)°. The distortion from regular symmetry about C-7 may in part be caused by non-bonded interactions between the methylene hydrogen

Oxygen–hydrogen non-bonded contacts, shorter than the sum of the respective van der Waals radii, 2·60 Å,[12] are observed in the environments of both spiro-carbon atoms, as shown in Table 2(d), and these could also be
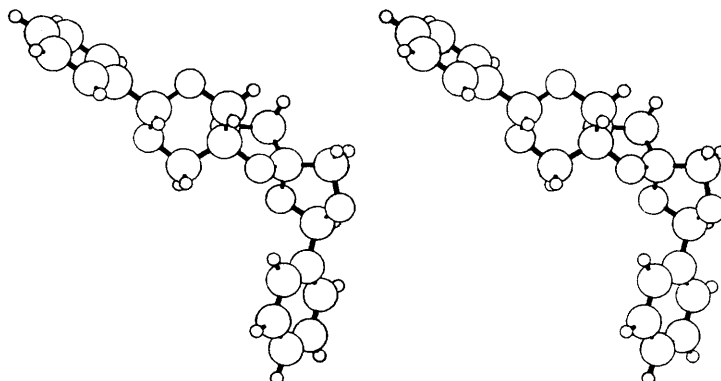

FIGURE 1   A stereodrawing of the molecule of 2,10-diphenyl-1,3,6,9,11,13-hexaoxadispiro[4.1.5.2]tetradecane

Angles not shown
in figure:

C8-C7-O13	109·8(3)
C12-C7-O6	108·5(2)
C4-C5-O6	110·5(3)
C14-C5-O1	112·0(2)
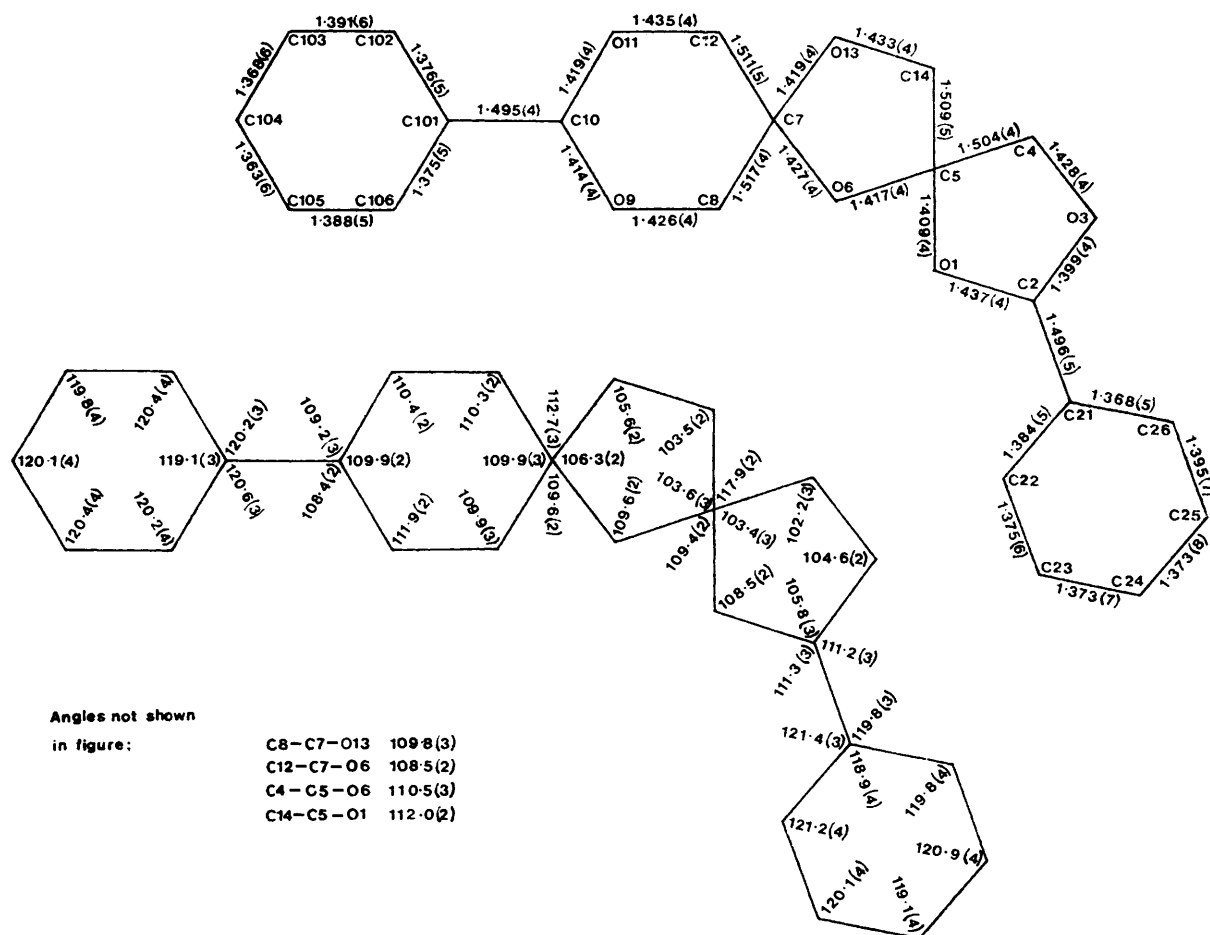
FIGURE 2   A schematic drawing of the molecule showing the labelling of the atoms and the intramolecular bond lengths and angles, with estimated standard deviations in parentheses

atoms at C-12 and C-14 since the distance between H-12eq and H-14 is 2·47 Å, which is only slightly greater than the van der Waals diameter of the hydrogen atom, i.e. 2·4 Å.[12]

responsible for distortions in the geometries about the spiro-carbon atoms. It has been suggested that close

[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Oxford University Press, 1960.

TABLE 2

(a) Equations of least-squares planes and distances (Å) of atoms from the planes *

Plane (i): C(101), C(102), C(103), C(104), C(105), C(106)

$$0.7780X - 0.3009Y + 0.5516Z + 0.0600 = 0$$

C(101) 0.002, C(102) —0.001, C(103) 0.001, C(104) —0.002, C(105) 0.003, C(106) —0.002, C(10) 0.016

Plane (ii): C(8), O(9), O(11), C(12)

$$0.3141X + 0.9315Y + 0.1834Z - 7.9961 = 0$$

C(8) —0.005, O(9) 0.005, O(11) —0.005, C(12) 0.005, C(7) —0.639, C(10) 0.680

Plane (iii): C(5), O(6), C(7), O(13), C(14)

$$0.7235X - 0.5417Y + 0.4279Z + 2.2844 = 0$$

C(5) 0.124, O(6) —0.018, C(7) —0.104, O(13) 0.189, C(14) —0.191

Plane (iv): O(1), C(2), O(3), C(4), C(5)

$$0.3891X + 0.7825Y + 0.4860Z - 6.1952 = 0$$

O(1) —0.009, C(2) —0.130, O(3) 0.224, C(4) —0.217, C(5) 0.132

Plane (v): C(21), C(22), C(23), C(24), C(25), C(26)

$$0.1367X + 0.5732Y - 0.8079Z - 1.7863 = 0$$

C(21) —0.012, C(22) 0.007, C(23) 0.007, C(24) —0.016, C(25) 0.012, C(26) 0.002, C(2) —0.033

Dihedral angles between normals to planes (deg.)

Planes		
(i) and (ii)	86.3
(ii) and (iii)	101.5
(iii) and (iv)	86.2
(iv) and (v)	83.7

* X, Y, and Z refer to orthogonal co-ordinates (Å) obtained by the transformation

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a\sin\beta & 0 & 0 \\ 0 & b & 0 \\ a\cos\beta & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

(b) Torsion angles (deg.) for the 1,3-dioxan ring

C(7)—C(8)—O(9)—C(10)	—57.1
C(8)—O(9)—C(10)—O(11)	63.5
O(9)—C(10)—O(11)—C(12)	—63.5
C(10)—O(11)—C(12)—C(7)	58.3
O(11)—C(12)—C(7)—C(8)	—51.8
C(12)—C(7)—C(8)—O(9)	50.8

(c) Torsion angles (deg.) and pseudo-rotational parameters for the dioxolan rings

Ring (i): O(1), C(2), O(3), C(4), and C(5)

C(2)—O(3)—C(4)—C(5)	39.8	ϕ_0
O(1)—C(2)—O(3)—C(4)	—32.9	ϕ_1
C(5)—O(1)—C(2)—O(3)	12.3	ϕ_2
C(4)—C(5)—O(1)—C(2)	12.1	ϕ_3
O(3)—C(4)—C(5)—O(1)	—31.5	ϕ_4

Pseudo-rotational phase angle, $P = 0.8$

Ring (ii): C(5), O(6), C(7), O(13), and C(14)

C(7)—O(13)—C(14)—C(5)	34.2	ϕ_0
O(13)—C(14)—C(5)—O(6)	—28.3	ϕ_1
C(14)—C(5)—O(6)—C(7)	12.2	ϕ_2
C(5)—O(6)—C(7)—O(13)	8.6	ϕ_3
O(6)—C(7)—O(13)—C(14)	—27.2	ϕ_4

Pseudo-rotational phase angle, $P = 2.6$

(d) Important intramolecular O · · · H separations (Å)

O(1) · · · H(4)	3.15	O(6) · · · H(12)	2.65
O(1) · · · H(4')	2.74	O(6) · · · H(12')	2.52
O(1) · · · H(14)	2.52	O(6) · · · H(14)	3.15
O(1) · · · H(14')	3.26	O(6) · · · H(14')	2.78
O(6) · · · H(4)	2.50	O(13) · · · H(8')	3.26
O(6) · · · H(4')	3.25	O(13) · · · H(8)	2.54
O(6) · · · H(8')	2.56	O(13) · · · H(12)	2.60
O(6) · · · H(8)	2.71	O(13) · · · H(12')	3.28

contacts of this type cause distortions of the spiro-linkages in 7,8,15,16-tetraoxadispiro[5.2.5.2]hexa-decane,[13] 8,9,17,18-tetraoxadispiro[6.2.6.2]octadecane,[14] and 9,10,19,20-tetraoxadispiro[7.2.7.2]eicosane.[15]

Quantitative descriptions of the conformations of five-membered rings have been made using the concept of pseudorotation.[16] A specific phase angle, P, which is a function of the five torsion angles in the ring (ϕ_0—ϕ_4 inclusive) locates the exact position of the observed conformation on the pseudorotation pathway. The value of P is dependent on the choice of a standard conformation, although a change in this choice merely rotates P by a multiple of 36° (this is only strictly true for cyclopentane rings). For the furanose rings in nucleosides and nucleotides [17] the standard conformation ($P = 0°$), is characterised by a maximally positive torsion angle opposite the oxygen atom in the ring. Following this description we choose the torsion angles C-2-O-3-C-4-C-5 and C-5-C-14-O-13-C-7 as ϕ_0 for the two respective dioxolan rings in the present compound. The values of the pseudorotation parameters, $P = 0.8°$ for the dioxolan ring involving O-1 and O-3 and $P = 2.6°$ for the second ring involving O-6 and O-13, show that for both rings the geometry is essentially the symmetrical twist (T) conformation. In terms of displacements of atoms from planes, O-3 and C-4 are displaced out of the plane defined by O-1, C-2, and C-5 by 0.29 and —0.31 Å respectively, whereas O-13 and C-14 are displaced out of the plane defined by C-5, O-6, and C-7 by —0.20 and 0.32 Å respectively.

The dioxan ring adopts the chair conformation in which the atoms C-7 and C-10 are displaced by —0.64 and 0.68 Å respectively from the least-squares plane through the atoms C-8, O-9, O-11, and C-12. The carbon–carbon and carbon–oxygen bond lengths are normal in both the dioxan and dioxolan rings with average values of 1.510 and 1.422 Å respectively. Both phenyl rings are planar within experimental error with an average carbon–carbon bond length of 1.377 Å.

Figure 3 is a stereoview of the unit cell contents looking along the c axis. The molecules lie approximately in planes perpendicular to the b axis which is consistent with the pronounced tabular habit of the crystals parallel to the {010} face. There are no intermolecular separations significantly less than the sum of the respective van der Waals radii.

EXPERIMENTAL

The n.m.r. spectra were measured on a Varian A-60D or a JEOL JMN-MH-100 instrument, and 220 MHz spectra were measured by the P.C.M.U. at Harwell on a Varian HA 220. I.r. spectra were measured with a Perkin-Elmer Infracord model 13. G.l.c. was carried out with a Varian-Aerograph 200A instrument with hydrogen as carrier gas,

[13] P. Groth, Acta Chem. Scand., 1967, 21, 2608.

[14] P. Groth, Acta Chem. Scand., 1967, 21, 2631.

[15] P. Groth, Acta Chem. Scand., 1967, 21, 2695.

[16] J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, J. Amer. Chem. Soc., 1947, 69, 2483.

[17] C. Altona and M. Sundaralingam, J. Amer. Chem. Soc., 1972, 94, 8205.

a thermal conductivity detector, and a column (10 ft × ¼ in) packed with 20% SE30 on Chromosorb W (60—80 mesh). Molecular weights were determined with a Mechrolab vapour pressure osmometer model 301A.

Ruthenium Tetraoxide Oxidation of cis-trans-2-*Phenyl*-1,3-*dioxan*-5-*ol* (1).—A solution of ruthenium tetraoxide in carbon tetrachloride, which had been prepared in the usual way from ruthenium dioxide hydrate (5·8 g),[3] was dried over anhydrous calcium sulphate and then added under anhydrous conditions to a stirred solution of a *cis–trans* mixture of 2-phenyl-1,3-dioxan-5-ol (1) (10 g) in carbon tetrachloride (120 ml). After 2 h, g.l.c. analysis at 165° showed that the alcohol (1) (R_t 6·0 min) had been converted into a product (R_t 4·3 min). The ruthenium dioxide was rapidly filtered off and the filtrate evaporated to low bulk (*ca.* 25 ml) and divided into two equal parts. From

piped-shaped fragment, cut from a large crystal, and of dimensions 0·396 × 0·116 × 0·264 mm parallel to *a*, *b*, and *c* respectively, was mounted about the *a* axis and used for the X-ray measurements. Preliminary unit cell parameters and space group information were obtained from Weissenberg and precession photographs. Refined cell parameters were obtained from the θ values of 20 reflections measured on a Hilger–Watts Y290 automatic four-circle diffractometer using Cu-K_{α_1} radiation (λ = 1·5405 Å). Intensity data were also measured on this instrument with the ω/2θ scanning technique, using Ni-filtered Cu-K_α radiation and a scintillation counter connected to a pulse-height analyser. Nickel foil attenuators were used to maintain measurements within the linear region of the scintillation counter.

3313 Independent reflections were measured in the range $0° \leqslant 2\theta \leqslant 140°$ including 1589 'insignificant' reflections
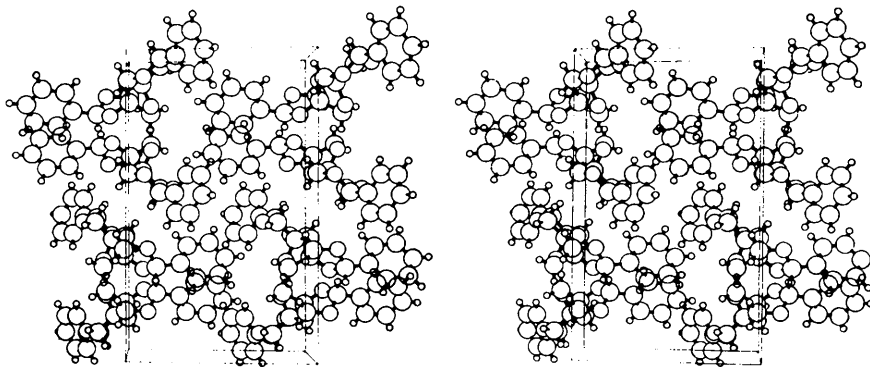

FIGURE 3   A stereoview of the unit cell contents looking along the *c* axis

one portion the remaining carbon tetrachloride was evaporated off to give an oil (3 g), $\nu_{max.}$ 1750 cm⁻¹ (C=O), which was then dissolved in moist ether (40 ml) and light petroleum (b.p. 40—60°) (3 ml). A crystalline sample of 2-phenyl-1,3-dioxan-5,5-diol (3) separated (2 g), m.p. 80—81° (lit.,[2] 81°), $\nu_{max.}$ (KBr) 3450 cm⁻¹ (OH), δ [(CD₃)₂CO] 4·40 (d, J_{gem} 16·0 Hz, CH₂), 4·54 (d, J_{gem} 16·0 Hz, CH₂), 5·99 (s, PhC*H*), 7·1— 7·7 (m, Ph), and 2·8br (s, OH), δ (CDCl₃) 4·40 (s, 2 × CH₂), 5·83 (s, PhC*H*), and 7·2—7·7 (m, Ph), $\nu_{max.}$ (CDCl₃) 1750s (C=O) and 3450vw cm⁻¹.

The second portion of the carbon tetrachloride solution was left at 0°, and after 24 h crystals appeared, which increased during 1 month. The solid was filtered off (3·1 g) and recrystallised from acetone to give pure 2,10-*diphenyl*-1,3,6,9,11,13-*hexaoxadispiro*[4.1.5.2]*tetradecane* (4), m.p. 137—138°, δ values recorded in Table 1, *m/e* 356 (0·5%, M⁺), 355 (1·1, M − 1; loss of a benzylidene methine proton), 220 {100, M − 136; loss of PhCHO and HCHO by cleavage *inter alia* of bonds 1—5 [see (4)] and 4—5}, 178 (8), 162 (35), 120 (18), 105 (100, C₆H₅$\overset{+}{C}$O), and 77 (71, C₆H₅⁺) (Found: C, 67·4; H, 5·6%; *M*, 345 (osmometer). C₂₀H₂₀O₆ requires C, 67·4; H, 5·7%; *M*, 356).

Crystal Data.—C₂₀H₂₀O₆, *M* = 356·4. Monoclinic, *a* = 11·160(2), *b* = 18·653(3), *c* = 8·674(1) Å, β = 99·485(3)°, *U* = 1781 Å³, D_c = 1·27, *Z* = 4, D_m = 1·27, *F*(000) = 752. Cu-K_α radiation, μ(Cu-K_α) = 7·90 cm⁻¹. The conditions limiting possible reflection, 0*k*0, *k* = 2*n* and *h*0*l*, *l* = 2*n* uniquely determine the space group as $P2_1/c$ (C_{2h}^5, No. 14).

The monoclinic crystals obtained by recrystallisation from acetone are colourless with a pronounced tabular habit parallel to the clinopinacoid {010} face. A parallele-

for which $I < 3\sigma(I)$; all the reflections were used in the analysis. Gradual variations in the experimental conditions were monitored throughout the data collection by measuring three reference reflections after every 50 reflections and the intensity data were scaled to these references. The intensity data were corrected for Lorentz and polarisation effects but no corrections were made for absorption. A set of normalised structure factors, E_h, was then computed from the observed structure factors.

Solution and Refinement of Structure.—Phases were determined for the 200 normalised structure factors with values of $E_h > 1·95$ by means of the tangent formula due to Karle and Hauptmann[18] modified by Germain, Main, and Woolfson.[19]

Reflections 0,13,8 ($|E_h| = 4·64$), 1,6,7̄ ($|E_h| = 3·51$), and 7,10,4̄ ($|E_h| = 3·44$) were chosen to define the origin, whereas reflections 6,7,4 ($|E_h| = 3·67$), 1,7,8 ($|E_h| = 3·36$), and 3,13,0 ($|E_h| = 3·11$) comprised the starting set of phases. The solution with values 180, 180, and 0° respectively for the phase angles of the starting set of reflections gave the highest value for the figure of merit[19] (1·15), and an *E*-map computed with this set of phases revealed all the non-hydrogen atoms in the structure. A structure factor calculation using the atomic parameters obtained from this *E*-map gave an *R* value of 0·326.

Three cycles of full-matrix least-squares refinement with all atoms treated isotropically reduced *R* to 0·167. A difference Fourier synthesis showed electron density maxima (0·3—0·6 e Å⁻³) corresponding to all the hydrogen atoms in

[18] J. Karle and H. Hauptman, *Acta Cryst.*, 1956, **9**, 635.
[19] P. Main, G. Germain, and M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

the structure. However, because of the diffuse nature of these maxima, hydrogen atoms were placed, in subsequent calculations, in calculated positions assuming a carbon–hydrogen bond length of 1·0 Å. No attempt was made to refine the positional or thermal parameters of the hydrogen atoms.

Further refinement, in which the thermal vibrations of the non-hydrogen atoms were treated anisotropically, proceeded by a partial full-matrix technique in order to conserve computing time. No more than 12 atoms (108 parameters) were refined in any one cycle although an overall scale factor was always refined. This refinement was continued until all the parameter shifts were less than the corresponding estimated standard deviations. A final cycle of refinement in which all 26 non-hydrogen atoms were refined anisotropically gave R values of 0·091 and 0·044 for all the reflections and the 1724 significant reflections respectively. All parameter shifts were then less than 0·5 of the corresponding estimated standard deviations.

Weights were assigned to the unscaled observed structure factors throughout the refinement according to a function of the type; $w = a_0$ for $|F_0| \leqslant 18\cdot0$, otherwise $w = [1 - \exp(-a_1 \sin^2 \theta/\lambda^2)]/(18\cdot0 + a_2|F_0| + a_3|F_0|^2)$. Values of $a_0 = 0\cdot01$, $a_1 = 20\cdot0$, $a_2 = 0\cdot50$, and $a_3 = 0\cdot002$ were used in the final cycle; the value of $|F_0| = 18\cdot0$ represents a threshold value for the insignificant intensity data. An analysis of this weighting scheme in terms of batches of increasing $\sin\theta/\lambda$ and $|F_0|$ showed a constancy in the values of $\Sigma w \Delta^2/n$ and the final value of R' $\{= [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{\frac{1}{2}}\}$ was 0·100 for all the reflections. A difference Fourier synthesis showed a maximum variation in the residual electron density of $\pm 0\cdot2$ e Å^{-3}.

Throughout the structure factor calculations the atomic scattering factors listed by Hanson et al.[20] were used. All computations were performed on the CDC 6400 and 6600 computers at the University of London Computer Centre.

TABLE 3

(a) Positional atomic parameters for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
O(1)	0·0869(2)	0·2898(1)	0·3943(3)
C(2)	0·1605(3)	0·2990(2)	0·2745(4)
O(3)	0·1134(2)	0·3590(1)	0·1885(3)
C(4)	−0·0138(3)	0·3570(2)	0·1932(4)
C(5)	−0·0166(3)	0·3338(2)	0·3585(3)
O(6)	−0·0043(2)	0·3938(1)	0·4601(3)
C(7)	−0·0845(3)	0·3863(2)	0·5715(4)
C(8)	−0·0136(3)	0·3951(2)	0·7353(4)
O(9)	−0·0954(2)	0·4002(1)	0·8451(2)
C(10)	−0·1768(3)	0·4574(2)	0·8090(4)
O(11)	−0·2532(2)	0·4447(1)	0·6626(2)
C(12)	−0·1812(3)	0·4436(2)	0·5399(4)
O(13)	−0·1329(2)	0·3159(1)	0·5524(3)
C(14)	−0·1299(3)	0·2971(2)	0·3928(4)
C(21)	0·2911(3)	0·3097(2)	0·3435(4)
C(22)	0·3278(4)	0·3664(2)	0·4430(5)
C(23)	0·4478(4)	0·3755(3)	0·5080(5)
C(24)	0·5338(4)	0·3277(3)	0·4752(6)
C(25)	0·4988(5)	0·2727(3)	0·3723(8)
C(26)	0·3770(4)	0·2631(2)	0·3070(6)
C(101)	−0·2565(3)	0·4611(2)	0·9334(4)
C(102)	−0·3218(4)	0·4020(2)	0·9665(5)
C(103)	−0·3933(4)	0·4050(3)	1·0834(6)
C(104)	−0·3995(4)	0·4672(3)	1·1653(5)
C(105)	−0·3350(4)	0·5258(2)	1·1333(4)
C(106)	−0·2637(4)	0·5232(2)	1·0167(4)

TABLE 3 (Continued)

(b) Anisotropic thermal parameters * U_{ij} ($\times 10^3$), for the non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	63(1)	65(1)	55(1)	35(2)	29(2)	8(2)
C(2)	72(2)	52(2)	53(2)	−6(3)	43(3)	−12(3)
O(3)	80(2)	68(1)	49(1)	24(2)	31(2)	−16(2)
C(4)	64(2)	68(2)	48(2)	15(3)	2(3)	−21(3)
C(5)	56(2)	47(2)	45(2)	4(2)	7(3)	−6(3)
O(6)	67(1)	56(1)	62(1)	−20(2)	41(2)	−39(2)
C(7)	53(2)	47(2)	50(2)	1(3)	20(3)	−12(3)
C(8)	52(2)	63(2)	55(2)	−3(3)	7(3)	8(3)
O(9)	55(1)	64(1)	49(1)	14(2)	11(2)	17(2)
C(10)	57(2)	52(2)	49(2)	4(3)	12(3)	0(3)
O(11)	52(1)	62(1)	50(1)	13(2)	1(2)	7(2)
C(12)	70(2)	56(2)	49(2)	11(3)	9(3)	−1(3)
O(13)	64(1)	49(1)	57(1)	−4(2)	30(2)	−24(2)
C(14)	57(2)	57(2)	55(2)	−8(3)	10(3)	−23(3)
C(21)	65(2)	48(2)	62(2)	5(3)	47(3)	3(3)
C(22)	67(2)	67(2)	82(3)	−30(4)	33(4)	2(4)
C(23)	72(3)	89(3)	89(3)	−5(5)	29(4)	−23(5)
C(24)	65(3)	108(4)	100(3)	51(6)	38(5)	−16(5)
C(25)	77(3)	98(4)	154(5)	24(7)	90(7)	48(5)
C(26)	91(3)	68(2)	113(3)	−21(5)	83(5)	18(4)
C(101)	49(2)	57(2)	51(2)	11(3)	11(3)	−1(3)
C(102)	78(3)	66(2)	85(3)	3(4)	51(4)	−12(4)
C(103)	72(3)	97(3)	87(3)	47(5)	46(4)	−5(4)
C(104)	77(3)	109(3)	56(2)	28(4)	32(4)	27(5)
C(105)	91(3)	86(3)	56(2)	−10(4)	35(4)	8(5)
C(106)	75(2)	68(2)	53(2)	−7(3)	23(3)	−1(4)

* In the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

(c) Positional and thermal * parameters for the hydrogen atoms

Atom	x/a	y/b	z/c	$U(\times 10^3)$
H(2)	0·156	0·255	0·205	64
H(4)	−0·054	0·405	0·169	66
H(4')	−0·057	0·321	0·115	66
H(8')	0·040	0·439	0·742	65
H(8)	0·042	0·352	0·763	65
H(10)	−0·133	0·503	0·804	59
H(12)	−0·234	0·434	0·437	65
H(12')	−0·141	0·492	0·533	65
H(14)	−0·127	0·244	0·379	65
H(14')	−0·206	0·315	0·323	65
H(22)	0·265	0·401	0·470	77
H(23)	0·475	0·419	0·579	91
H(24)	0·622	0·331	0·529	96
H(25)	0·563	0·239	0·346	107
H(26)	0·352	0·223	0·229	94
H(102)	−0·321	0·356	0·901	83
H(103)	−0·443	0·363	1·108	92
H(104)	−0·448	0·469	1·251	86
H(105)	−0·340	0·572	1·194	84
H(106)	−0·216	0·566	0·994	72

* The isotropic thermal parameters were obtained by adding 0·006 Å^2 to the isotropic value for the corresponding carbon atom.

The final atomic co-ordinates and thermal parameters are given in Table 3. The list of observed and calculated structure factors is contained in Supplementary Publication No. SUP 21028 (52 pp., 1 microfiche).†

† For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

[20] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.