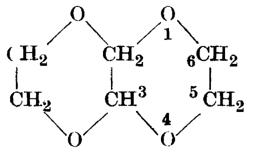
ACTA CHEMICA SCANDINAVICA 4 (1950) 1584–1596

Crystal Structure of ”*Cis*-Naphthodioxane” — Bi-1,3-Dioxacyclopentyl(2)

S. FURBERG and O. HASSEL

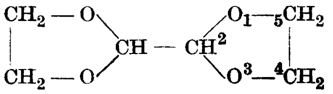
Universitetets Kjemiske Institutt, Blindern — Oslo, Norway

If ethylene glycol reacts either with 2,3-dichlorodioxane or with glyoxal two solid substances are obtained, one melting at 111° the other at 136° C (Böeseken, Tellegen and Cohen Henriquez [1]). Both substances have been assumed to be "naphthodioxanes" (I) and to correspond to the two stereoisomeric decalins.



(I)

Böeseken and co-workers have also, however, considered the possibility that one of the two substances might have the formula



(II)

but subsequently rejected this possibility on the basis of chemical arguments. The dipole moment of the higher melting isomer ("*trans*") was found to be very small (0.7 D), that of the lower melting substance ("*cis*"), however, was found equal to 1.7 D. In order to account for a moment of this magnitude "movable" forms of the dioxane rings had to be assumed.

We have considered this problem important in connection with earlier work on six-membered rings carried out in our laboratory, and have therefore undertaken crystallographic investigations of the two isomers in question.

PREPARATION OF THE SUBSTANCES

The substances were prepared from 2,3-dichlorodioxane and ethylene glycol using benzene as a solvent. In most cases a mixture of the two isomeric 2,3-dichlorodioxanes was used, but in one case the pure solid isomer of m. p. 32° C was employed. The proportion of higher and lower melting isomers in the reaction product seemed, however, to be the same in both cases, in conformity with the result obtained by Baker and Shannon [2]. By recrystallisation it was easy to isolate considerable quantities of the 136° isomer in a pure state. In addition a mixture of both isomers, melting at about 90°, was obtained, from which the lower melting substance could be isolated, although with some difficulty. The isolation could be performed either by partially melting the mixture and separating the solid part from the liquid, or by dissolving the mixture in water and slowly evaporating the solvent. In the latter case good single crystals of both isomers were obtained which might be separated by hand under the microscope.

In one case a solution from which the greater part of the higher melting isomer and a mixture of both isomers had already been removed, on further concentration yielded large needles apparently different from crystals of the higher melting substance. X-ray diagrams revealed an identity period of 4.46 Å along the needle axis. Weissenberg photographs recording reflexions on the first and second layer lines proved, however, that the needles were twins and not true single crystals. Later diagrams of well developed single crystals of the lower melting isomer showed that the needle-shaped crystals had the lattice of this isomer.

The formation of mixed crystals containing both isomers was not observed, neither by crystallisation from solutions nor by sublimation.

As pointed out in a preliminary communication [3], a complete crystal structure determination of the higher melting isomer does not appear promising. The crystal structure of the lower melting isomer, on the other hand, could more easily be carried out, and a detailed report of this investigation is given below.

MORPHOLOGY, UNIT CELL AND SPACE GROUP

The crystals are monoclinic, and may occur in different habits, either as plates (100) with b and c along the diagonals of a rhombus, or as plates (010) elongated along the a axis. Needle-shaped twins elongated along the a axis were also observed (see above).

From X-ray oscillation photographs the following unit cell dimensions were derived: $a = 4.46$ Å, $b = 7.76$ Å and $c = 11.64$ Å (all $\pm$ 1 %). Copper ($\lambda = 1.54$ Å) and iron ($\lambda = 1.934$ Å) radiation were used. The monoclinic angle β was obtained from a Weissenberg photograph about the b axis, and found equal to 121.5°. By flotation of the crystals in a mixture of benzene and carbon tetrachloride a density of about 1.40 g/cm^3 was measured, corresponding to *two* (calc. 1.97) molecules $C_6H_{10}O_4$ in the unit cell.

Systematic absences occur in the *h*0*l* reflexions for odd values of *l*, and in the 0*k*0 reflexions for odd values of *k*. The space group is therefore $P2_1/c$, from which follows that the molecule must be centrosymmetrical, with its centre of symmetry in special positions in the unit cell.

DETERMINATION OF THE STRUCTURE FACTORS $F_{obs.}$

A needle-shaped crystal elongated along *a* and with a cross-section of 0.4 × 0.4 mm was used to take a series of Weissenberg photographs recording the 0*kl* reflexions. The compound is volatile and was therefore kept in a thin-walled glass capillary tube. Exposure times varied between 2 h and 60 h. 75 of the 97 reflexions attainable with Cu $K\alpha$ radiation were recorded on the film with measureable intensity. The intensities were estimated visually and corrected for the Lorentz polarization factor, using the method of Goldschmidt and Pitt [14]. No correction was applied for absorption or extinction. Later on, the values were converted to an approximately absolute scale by comparison of observed and calculated structure factors.

For the *b* axis photographs a tabular crystal with a cross-section of roughly 0.1 × 0.6 mm was used. The shape of the reflected beams as recorded on the film showed great variations, and a correction for this "spot shape" effect had to be applied, following the procedure described by Broomhead [4]. It was found that the observed intensities had to be multiplied by factors varying between 1.0 and 0.5, taking the factor 1.0 for beams leaving the crystal perpendicularly to the dominating face (100). 43 of the 55 *h*0*l* reflexions theoretically available were recorded.

ATTEMPTS TO DETERMINE THE STRUCTURE USING THE NAPHTHODIOXANE FORMULA

A crystal structure determination was first attempted using the naphthodioxane formula (I). As mentioned in the preliminary report [3] it was found impossible to work out a satisfactory structure along these lines, but we would nevertheless like to include a brief account of the trials, as we think they elucidate certain fundamental aspects of crystal structure determination.

Because of the shortness of the *a* axis, the projection in the direction of this axis was first considered. An approximate structure was soon found, which gave a fairly good agreement between observed and calculated structure factors for the low order reflexions. A Fourier synthesis was carried out, giving a promising electron density map, which improved during the following four refinements. In the course of this process the value of $R = \Sigma||F_{obs.}| - |F_{calc.}|| / \Sigma|F_{obs.}|$ decreased gradually from about 0.55 to 0.38, when no more sign changes occurred. The final electron density map is shown in Fig. 1. The two condensed six-membered rings appear clearly on the map, with all the atoms well resolved and with peak heights corresponding about to 5e.Å^{-2} for the three carbon atoms

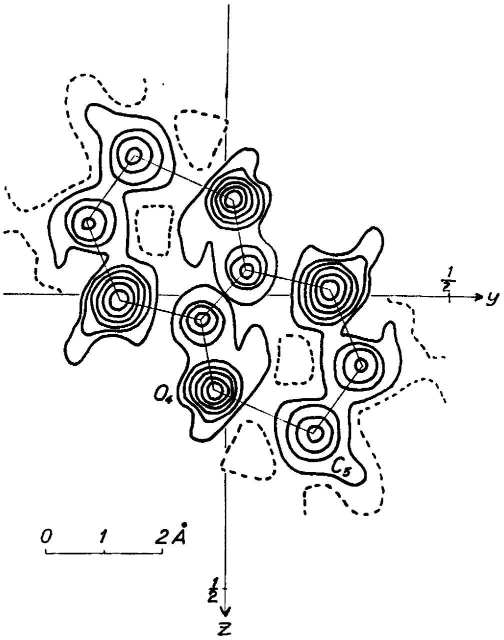


Fig. 1. Electron density map obtained by using the naphthodioxane formula. Contours at intervals of 1 e. Å^{-2}, the unit contour line being dotted.

and 7 e. Å^{-2} for the two oxygen atoms. However, the structure cannot be the correct one for the following reasons:

1) The agreement between $F_{obs.}$ and $F_{calc.}$ is not satisfactory. The value 0.38 for the reliability factor R is too high for a structure of this type, although it is low enough to indicate that the structure might be *essentially* correct. (As will be shown later, an R-value of 0.13 was obtained for the correct structure.)

2) The distance between the peaks corresponding to the atoms O_4 and C_5 is 1.80 Å, a value which is not compatible with our present knowledge of bond lengths in organic compounds.

3) Small spurious peaks and distortions occur in the electron density map shown in Fig. 1.

Many more trials were carried out with naphthodioxane models, but we never succeeded in getting values of R below 0.38. However, it is not safe to conclude from these negative results that the substance cannot be an isomer of naphthodioxane. The definite proof of this was obtained by the subsequent finding of a structure, against which the objections in 1), 2) and 3) cannot be raised.

THE STRUCTURE DETERMINATION BASED ON THE BI-DIOXA*CYCLO*-PENTYL (2) FORMULA

Our failure of establishing the crystal structure on the basis of the naphthodioxane formula made us consider the possibility, that the substance might be bi-1,3-dioxa*cyclo*pentyl(2), although the chemical evidence, as interpreted by Böeseken *et al.* [1], has not substantiated this view.

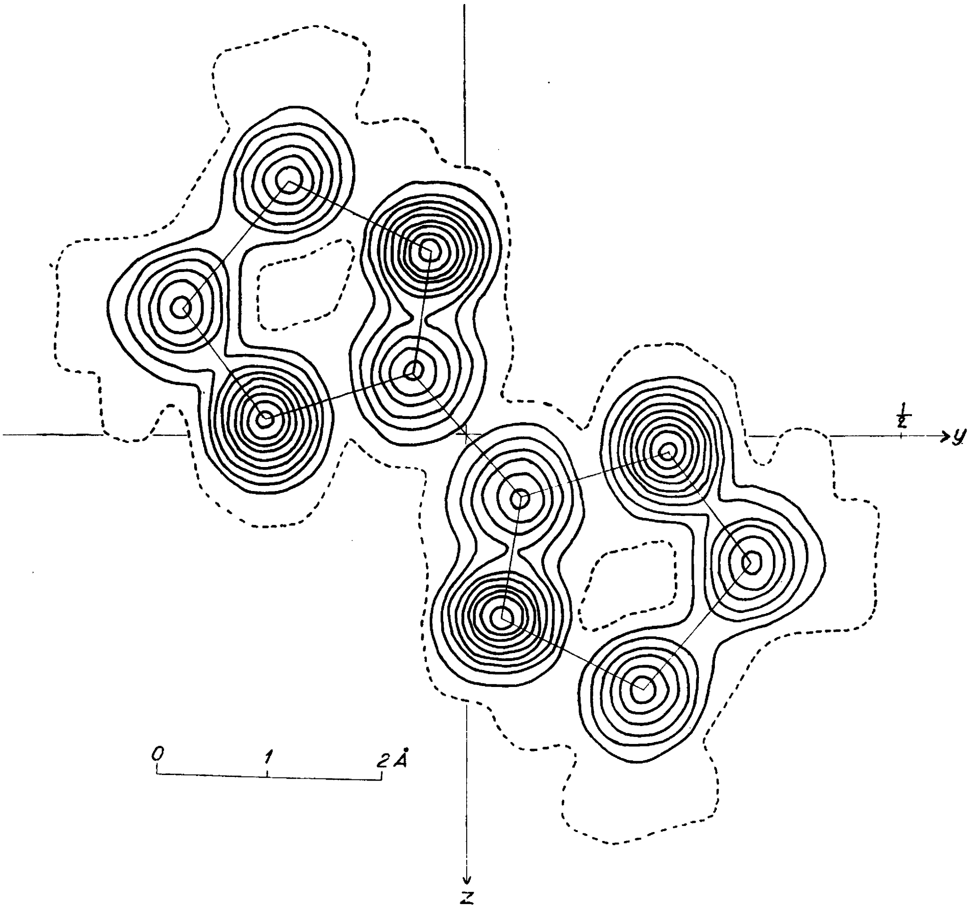


Fig. 2. Fourier projection in direction of a axis. Contours at intervals of 1 e. Å^{-2}, the unit contour line being dotted. The electron density is calculated at 1/60th of b and c axes.

a axis projection. It will be seen from models that molecules corresponding to the formulae (I) and (II) may be very similar in projection, except for the position of the atom C_2. Indeed, the first postulated co-ordinates based on the bi-dioxa*cyclo*pentyl formula (II) differed from the original structure postulated for (I) only in the y co-ordinate of the atom C_2, which was changed from $-y_2$ to $+y_2$. The factor R was about the same in both cases (0.55), but whereas the refinement could not be improved beyond $R = 0.38$ if (I) was used, the value 0.13 was reached if the calculations were based on (II).

The resulting electron density map (Fig. 2) has reasonable inter-peak distances and no unexplainable peaks or distortions. The three carbon atoms

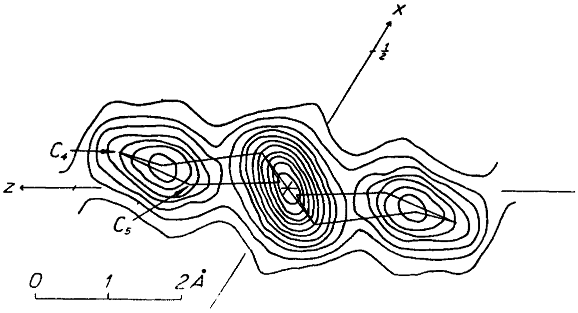


Fig. 3. Fourier projection in direction of b axis. Contours at intervals of 2 e. Å^{-2}.

have almost identical peak heights (7.1 ± 0.1 e. Å^{-2}) and the same holds for the two oxygen atoms (10.4 ± 0.1 e. Å^{-2}). All the atoms are well resolved, and their co-ordinates may be derived directly from the map. The presence of hydrogen atoms at C_4 and C_5 is also indicated.

In the first stages of the analysis the experimental values of the atomic scattering factor f given by Robertson [5] for hydrocarbons were used, weighting oxygen and carbon as 8 to 6. No separate account was taken for the hydrogen atoms. In this way an R-value of 0.17 was obtained. When inserting the hydrogen atoms in the positions which appeared reasonable, the agreement became no better. In view of the relatively great importance of the oxygen atoms in the structure, the theoretical Hartree f-curves (see *International Tables*) should be expected to be more satisfactory. The structure factors thus obtained gave an R-value of 0.16, and now the influence of the hydrogen atoms was very noticeable, as their inclusion made R drop to 0.13. It is interesting to notice that the introduction of more accurate f-curves made one reflexion (034) change sign, which again caused displacements of about 0.01 Å for the atoms O_1 and C_4. Inaccurate f-values *may* thus lead to errors in the co-ordinates.

When using the theoretical f-curves a temperature factor $e^{-B\,(\sin\,\Theta/\lambda)^2}$ must of course be introduced. The value of B was found to be 3.2 Å^2 by comparison of observed and calculated structure factors.

By the calculation of the reliability factor R the reflexions which are too weak to be observed, were treated in the following way: If $F_{\text{calc.}}$ is less than the lowest observable value of $F_{\text{obs.}}$, the error is taken equal to zero. If $F_{\text{calc.}}$ is greater, the error is taken as the difference between $F_{\text{calc.}}$ and the smallest value of $F_{\text{obs.}}$. In $\Sigma|F_{\text{obs.}}|$ the non-observed reflexions are not included.

In Table 3 $F_{\text{obs.}}$ and $F_{\text{calc.}}$ are compared for all $0kl$ and $h0l$ reflexions available with Cu $K\alpha$ radiation.

b axis projection. The knowledge of the z co-ordinates and approximate bond lengths made it easy to work out this projection, and after only two approximations the final electron density map shown in Fig. 3 was obtained. As the peaks overlap extensively, it is not possible to derive very accurate co-ordinates from the map. The x co-ordinates were determined by finding the maxima of electron density along lines corresponding to the known z co-ordinates, the influence of the neighbouring peaks being roughly corrected for by subtracting them from the map, using the standard shape of the Fourier peak as given in a paper by Booth [6]. Obviously the procedure is not very satisfactory, and the x co-ordinates can only be given to two-figure accuracy (see Table 1).

The structure factors were first calculated using the Hartree f-curves with the same temperature factor as in the a projection ($B = 3.2$). This gave good agreement between $F_{\text{obs.}}$ and $F_{\text{calc.}}$ for planes roughly parallel to (001). However, for all other planes $F_{\text{obs.}}$ was decreasing much more rapidly with increasing Θ than $F_{\text{calc.}}$, and for planes approximately perpendicular to (001) the value of $B = 5.2$ was found. This is believed to be due to oriented thermal vibrations of the molecule; it lies roughly in the (100) plane and would therefore be expected to vibrate chiefly in a direction normal to this plane. In accordance with this view (100) gives a strongly diffuse reflexion on Laue photographs. The temperature factor depends consequently not only on sin Θ/λ but also on the orientation of the plane in question. In order to account for this, the reciprocal lattice was divided in sectors, and B-values varying between 3.2 and 5.2 were assigned to the sectors by comparison of observed and calculated structure factors for high values of Θ.

Table 1. Atomic co-ordinates as fractions of the corresponding cell edge.

Atom	x	y	z
O_1	0.04	0.232	0.015
C_2	0.13	0.061	0.055
O_3	0.08	0.040	0.164
C_4	0.13	0.201	0.228
C_5	0.015	0.328	0.114

The reliability factor for the b axis projection is 0.17, being reduced to 0.16 when inserting the hydrogen atoms.

Discussion of errors. The co-ordinates derived from electron density maps are liable to errors from different sources, especially when only two-dimensional methods are used, as in the present case.

Errors in $F_{\text{obs.}}$ are shown by Booth [6,7] and Robertson [8] to be of minor importance, in general leading to displacements in the peak positions of less than 0.01—0.02 Å. This was substantiated in the present case by an independent determination of $F_{\mathrm{obs.}}$ for the $0kl$ reflexions, using Fe $K\alpha$ radiation (Cu radiation was not available when the investigation was started), another crystal specimen (cross-section 0.05 × 0.13 mm), the intensity estimations being carried out by an independent observer. The agreement between the two sets of $F_{\mathrm{obs.}}$ was satisfactory, the mean difference between the two observations being 0.9, or in general 10 − 15 %. This was found to cause deviations of 0.01 − 0.04 Å in the peak positions on the Fourier map (reflexions not available with Fe radiation were taken from diagrams obtained with Cu radiation). These deviations are somewhat greater than those quoted by Booth and Robertson, which was also to be expected because different radiations were used.

The finite summation errors were investigated following the procedure described by Booth [6]. It was found that these errors cause atomic displacements varying from 0.01 to 0.035 Å, but application of these corrections did not give better agreement between $F_{\mathrm{obs.}}$ and $F_{\mathrm{calc.}}$. It is thus hardly possible to decide whether the corrected co-ordinates are better than the original ones or not.

Overlapping of peaks and thermal vibrations give rise to very considerable errors in the x co-ordinates, which, it is believed, may possibly be as great as 0.06 Å. However, the molecule lies roughly in the (100) plane, and errors in the x co-ordinates do not influence the bond lengths appreciably. Considering the different sources of errors, we think that the maximum possible error in the bond lengths may be about 0.06 Å, but that it is likely to be smaller, say 0.03 Å.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The molecular structure. The bond lengths calculated from the co-ordinates in Table 1 are given in Table 2, column I. After correction for finite summation errors the values in column II were obtained. It will be seen that the four independent determinations of the C—O bond agree very closely with the generally accepted value (1.42 Å) for a normal single bond, their mean value being 1.41 Å. The deviations of the two C—C bond lengths from the standard value 1.54 Å are also well within the limits of error. As for the bond angles, their deviations from the value 108—109° are not believed to be significant, except for the angles at C_4 and C_5 which are as small as 102° and 104° respectively.

Table 2. Bond lengths (in Ångström units) and bond angles.

Bond	I	II	Angle	
C_2-O_3	1.407	1.414	$\angle\ C_2'C_2O_3$	106°
O_3-C_4	1.408	1.413	$\angle\ C_2'C_2O_1$	111°
C_5-O_1	1.420	1.416	$\angle\ O_1C_2O_3$	105°
O_1-C_2	1.394	1.402	$\angle\ C_2O_3C_4$	109°
C_4-C_5	1.507	1.534	$\angle\ O_3C_4C_5$	102°
C_2-C_2'	1.523	1.523	$\angle\ C_4C_5O_1$	104°
			$\angle\ C_5O_1C_2$	111°

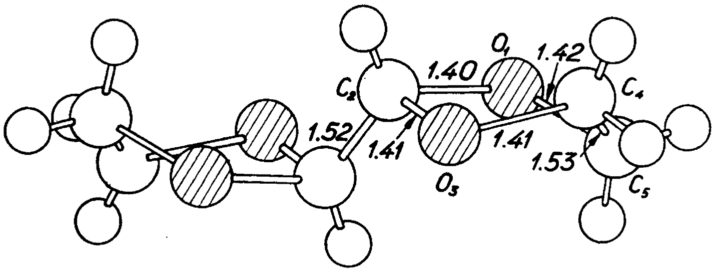


Fig. 4. A model of the molecule, with bond lengths (in Å units).

A plane defined by the three atoms O_1, C_2 and O_3 do not pass through either C_5 or C_4, the distances from these atoms to the plane being about 0.25 Å and 0.6 Å respectively. C_4 and C_5 lie on the same side of the plane. Because of the inaccuracy of the x co-ordinates, the displacement of C_5 from the plane may not be significant, whereas C_4 definitely appears to be out of the rough plane through the four other atoms. Thus the five-membered ring would seem to deviate from a planar ring in roughly the same way as described earlier for fructofuranose [9] and *d*-ribose [10].

The deviation from planarity is probably due mainly to repulsive forces between the hydrogen atoms. With a planar ring the hydrogen atoms at C_4 and C_5 are in *cis* position and only 2.25 Å apart. It will be seen by means of models (compare Fig. 4) that by moving the atom C_4 out of the plane of the ring by about 0.5 Å, the hydrogen atoms will approximately be brought into *trans* position, with a separation of 2.4—2.5 Å, a distance corresponding to the sum of the van der Waals radii. It appears therefore that favourable H—H distances are most easily obtained by a deformation of the five-membered ring from the planar model. The great importance of forces acting between non-bonded atoms has earlier been demonstrated in the case of six-membered rings (cyclohexane and related substances) [13].

The packing of the molecules. The shortest intermolecular atomic distances are those between the atom O_3 and the atoms C_4 and C_5, the separation being 3.25 Å in both cases (see Fig. 5). This is somewhat shorter than the distances found between oxygen atoms and methylene groups in glycine [11] (3.38 Å, 3.52 Å) and diketopiperazine [12] (3.32 Å, 3.33 Å). The distances from the oxygen atom O_1 to C_4 and C_5 in different neighbouring molecules are 3.57 Å and 3.68 Å. Unfortunately only very approximate positions of the hydrogen atoms can be given, but calculations seem to indicate (compare Fig. 5) that neighbouring atoms belonging to different molecules are separated by distances corresponding roughly to the normal values of the van der Waals radii (1.2 Å for hydrogen atoms and 1.4 Å for oxygen atoms).

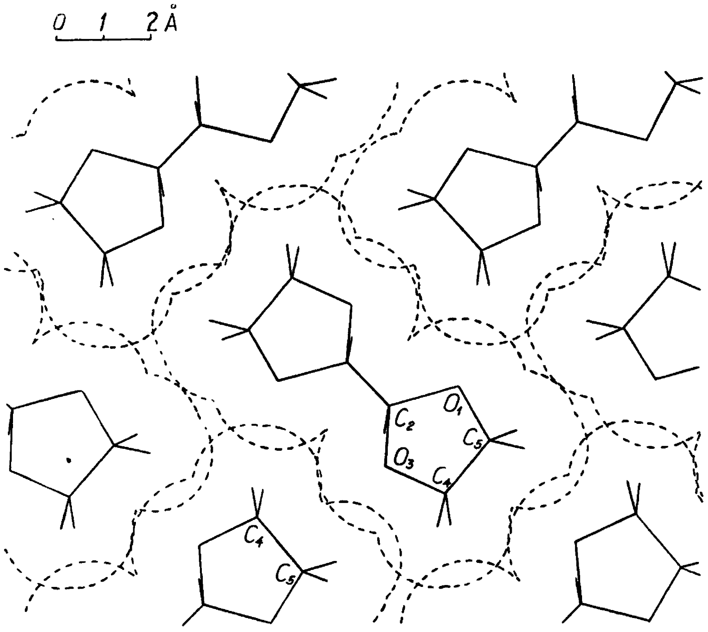
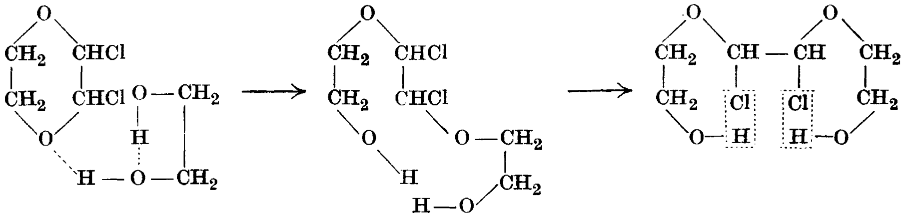


Fig. 5. The crystal structure projected in direction of a axis. Van der Waals contacts are shown dotted.

CHEMICAL ASPECTS

Since the structure analysis has established beyond doubt that the lower melting isomer is bi-1,3-dioxa*cyclo*pentyl(2), a few remarks on the possible reactions leading to this product would perhaps be of interest.

It is easy to understand that both isomers ((I) and (II)) may be formed by the reaction between glyoxal and ethylene glycol. The formation of five-membered rings from 2,3-dichlorodioxane and ethylene glycol seems, however, more difficult to explain. At least two possibilities would appear to deserve consideration. In the first place the reaction may start for example with a complex containing two hydrogen bonds according to the scheme:



Secondly, if not both the solvent and the ethylene glycol are completely free from traces of water, the primary process may be a hydrolysis of 2,3-dichlorodioxane giving (besides glycol) a quantity of glyoxal equivalent to the amount of water originally present. Bi-1,3-dioxa*cyclo*pentyl(2) would then be formed by the reaction between *glyoxal* and ethylene glycol, a process which again yields water, thus enabling the reaction to continue.

Table 3. Comparison of observed and calculated structure factors.

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
002	9.7	+ 10.4
004	8.0	+ 6.1
006	10.6	+ 10.0
008	3.5	+ 4.3
0 0 10	1.6	− 1.5
0 0 12	1.9	+ 0.7
011	22.3	+ 25.7
012	28.5	− 33.4
013	6.7	− 8.7
014	5.0	− 7.3
015	11.7	+ 11.1
016	6.0	− 4.9
017	< 1.4	+ 0.1
018	< 1.4	− 0.9
019	7.1	− 8.6
0 1 10	4.8	− 6.6
0 1 11	< 1.3	− 1.3
0 1 12	< 1.0	− 0.7
020	13.8	− 12.5
021	12.6	− 15.1
022	7.3	− 9.8
023	8.1	+ 8.0
024	20.8	− 24.7
025	7.1	− 7.0
026	3.2	+ 2.9
027	8.5	− 8.9
028	10.1	− 12.5
029	2.1	− 1.4
0 2 10	5.7	− 6.2
0 2 11	2.7	+ 3.5
0 2 12	1.4	+ 0.9
031	14.9	+ 12.9
032	13.6	− 15.2
033	17.9	− 17.6
034	2.7	+ 3.2
035	8.9	− 8.2
036	3.0	+ 2.5
037	3.5	+ 3.3
038	4.1	− 3.2
039	4.8	− 4.1
0 3 10	5.1	+ 6.3
0 3 11	< 1.2	+ 1.1
040	22.5	+ 20.4
041	8.6	− 7.8
042	4.8	+ 4.8
043	17.5	− 16.3
044	10.6	+ 10.0
045	9.4	+ 8.8
046	9.4	+ 8.9
047	4.2	− 3.8
048	< 1.5	+ 1.4
049	< 1.4	+ 1.1
0 4 11	2.1	+ 1.6
0 4 10	< 1.2	− 0.3
051	3.9	+ 3.5
052	10.2	− 9.7
053	< 1.4	+ 0.7
054	< 1.4	+ 0.5
055	9.0	+ 8.6
056	7.7	− 7.7
057	< 1.5	+ 0.4
058	6.9	− 7.1
059	1.8	+ 1.7
0 5 10	1.7	+ 1.7
060	4.1	− 3.6
061	11.5	− 12.4
062	8.4	− 8.5

hkl	$F_{\text{obs.}}$	$F_{\text{calc.}}$
063	< 1.4	+ 0.6
064	8.0	− 7.3
065	2.5	− 2.5
066	4.2	− 3.3
067	4.6	− 4.4
068	< 1.4	+ 2.2
069	2.1	− 2.1
0 6 10	< 0.9	+ 1.2
071	8.5	− 8.4
072	8.5	− 8.5
073	3.7	− 2.5
074	3.0	+ 3.1
075	4.1	− 3.0
076	2.3	+ 1.7
077	< 1.3	+ 1.1
078	< 1.1	+ 0.5
079	0.9	− 0.7
080	5.8	− 6.5
081	< 1.4	+ 0.5
082	2.5	+ 2.4
083	< 1.4	+ 0.4
084	2.8	+ 1.9
085	3.5	+ 3.3
086	2.5	+ 2.8
087	2.1	− 2.5
091	1.9	+ 1.0
092	< 1.2	− 0.2
093	< 1.1	+ 0.9
094	< 1.0	+ 0.9
100	69.9	+ 79.0
102	6.1	− 7.1
104	5.2	+ 4.8
106	3.5	+ 2.1
108	< 2.0	+ 2.0
1 0 10	< 1.5	− 0.7
200	21.6	+ 24.2
202	6.2	− 7.5
204	< 2.0	+ 1.4
206	< 1.8	− 0.8
300	1.9	+ 1.8
302	2.6	− 3.0
304	< 1.8	− 0.9
306	< 1.2	+ 0.3
400	2.1	− 1.7
402	< 1.4	+ 0.0
$\bar{1}02$	30.3	+ 36.9
$\bar{1}04$	3.7	+ 3.5
$\bar{1}06$	24.0	+ 22.9
$\bar{1}08$	9.7	+ 9.7
$\bar{1}$ 0 10	< 2.0	+ 1.1
$\bar{1}$ 0 12	< 1.7	− 2.2
$\bar{2}02$	28.5	+ 28.8
$\bar{2}04$	5.9	− 4.6
$\bar{2}06$	24.2	+ 26.9
$\bar{2}08$	11.6	+ 13.9
$\bar{2}$ 0 10	4.1	+ 5.0
$\bar{2}$ 0 12	< 1.2	− 1.1
$\bar{2}$ 0 14	1.2	+ 0.9
$\bar{3}02$	12.7	+ 15.1
$\bar{3}04$	4.4	− 4.7
$\bar{3}06$	11.3	+ 11.2
$\bar{3}08$	11.9	+ 14.5
$\bar{3}$ 0 10	4.3	+ 6.6
$\bar{3}$ 0 12	2.6	+ 0.7
$\bar{3}$ 0 14	1.5	+ 1.1
$\bar{4}02$	2.3	+ 4.9
$\bar{4}04$	3.3	− 4.0
$\bar{4}06$	2.6	+ 1.1
$\bar{4}08$	7.3	+ 9.0
$\bar{4}$ 0 10	3.2	+ 5.5
$\bar{4}$ 0 12	2.5	+ 2.4
$\bar{4}$ 0 14	1.3	+ 1.0
$\bar{5}02$	< 1.5	+ 1.2
$\bar{5}04$	2.0	− 1.3
$\bar{5}06$	2.2	− 2.0
$\bar{5}08$	3.4	+ 4.0
$\bar{5}$ 0 10	1.7	+ 2.0
$\bar{5}$ 0 12	1.8	+ 1.7

SUMMARY

The crystal structure of "*cis*-naphthodioxane" m. p. 111° has been determined by two-dimensional Fourier syntheses. It is shown that the chemical formula assigned to this substance by Böeseken *et al.* is wrong; the compound is not an isomer of naphthodioxane, but bi-1,3-dioxa*cyclo*pentyl(2).

In the crystal the molecule has a centre of symmetry. Bond lengths in close agreement with the normal values (1.42 Å and 1.54 Å) for C—O and C—C single bonds are found. The five-membered ring appears to be non-planar, which is thought to be due to repulsion between hydrogen atoms belonging to neighbouring methylene groups.

We are very much indebted to Cand. real. E. Amble who has carried out most of the preparative work, but had to interrupt his investigation when he left this country for the United States. We also want to express our gratitude to Cand.polyt. M. Danö for her very valuable assistance during the first stages of the structure analysis. One of us (S. F.) wishes to thank *Norges Teknisk-Naturvitenskapelige Forskningsråd* for a grant.

REFERENCES

1. Böeseken, J., Tellegen, F., and Cohen Henriquez, P. *Recueil* **54** (1935) 733; *J. Am. Chem. Soc.* **55** (1933) 1284.
2. Baker, W., and Shannon, A. *J. Chem. Soc.* (1933) 1598.
3. Danö, M., Furberg, S., and Hassel, O. *Acta Chem. Scand.* **4** (1950) 965.
4. Broomhead, J. M. *Acta Cryst.* **1** (1948) 324.
5. Robertson, J. M. *Proc. Roy. Soc. A* **150** (1935) 106.
6. Booth, A. D. *Proc. Roy. Soc. A* **188** (1946) 77.
7. Booth, A. D. *Proc. Roy. Soc. A* **190** (1947) 482.
8. Robertson, J. M., and White, J. G. *Proc. Roy. Soc. A* **190** (1947) 329.
9. Beevers, C. A., and Cochran, W. *Proc. Roy. Soc. A* **190** (1947) 257.
10. Furberg, S. *Acta Cryst.* **3** (1950) 325.
11. Albrecht, G., and Corey, R. B. *J. Am. Chem. Soc.* **61** (1939) 1087.
12. Corey, R. B. *J. Am. Chem. Soc.* **60** (1938) 1598.
13. Hassel, O. *Research* **3** (1950) 504.
14. Goldschmidt, G. H., and Pitt, G. J. *J. Scien. Instr.* **25** (1948) 397.

Received November 17, 1950.