2450 © 1990 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 63, 2450—2451 (1990) [Vol. 63, No. 8

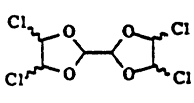
Crystal Structure of 4,4′,5,5′-Tetrachloro-2,2′-bi-1,3-dioxolane

Hsing Hua Huang, Koreharu Ogata,† Shin-ichiro Sakai,† and Keng Yeow Sim*
Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511
†Faculty of Pharmaceutical Sciences, Chiba University, 1-33 Yayoi-cho, Chiba 260

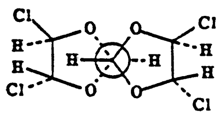
(Received October 17, 1989)

Synopsis. The main product, **A** obtained from the interaction of concentrated sulfuric acid with *trans*-2,3-dichloro-1,4-dioxane has been shown by a single crystal X-ray structure analysis to be the *trans-trans meso*-stereoisomer of 4,4′,5,5′-tetrachloro-2,2′-bi-1,3-dioxolane.

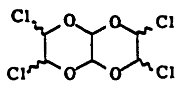
Cort[1] reported that the reaction of *trans*-2,3-dichloro-1,4-dioxane with hot concentrated sulfuric acid yielded a product, **A**, mp 143—144 °C and suggested it could be either 4,4′,5,5′-tetrachloro-2,2′-bi-1,3-dioxolane (**I**) or 2,3,6,7-tetrachloro-1,4,5,8-tetraoxadecalin (**II**). Later Huang[2] found that this reaction gave at least two compounds, **A**, mp 137—138 °C (presumed to be Cort's compound) and **B**, mp 83—86 °C. He showed by chemical and spectrometric studies that these two compounds were diastereoisomeric forms of structure (**I**) but was unable to assign their absolute stereochemistry. Five stereoisomers of **I** are possible: two *trans-trans* isomers (*meso* and (±)-*racemic*) and three *cis-cis* isomers (*endo-endo, exo-exo* and *endo-exo*). In an independent study on the structure of compound **A**, Fuchs and Hauptmann[3] reached a similar conclusion that it has the general structure (**I**) but were unable to clarify its stereochemistry. They also obtained a diastereoisomeric form of **I** mp 124—5 °C (also designated by them as compound **B**) from the addition of chlorine to 2,2′-bi-1,3-dioxolane which they assigned as the *cis, exo-cis, exo* isomer.



(I)



(Ia)



(II)

Experimental

Preparation of *meso*-4,4′,5,5′-Tetrachloro-2,2′-bi-1,3-dioxolane. The compound **A** was prepared according to the method of Cort[1] and recrystallized from acetone as prisms, mp 137—138 °C.

Crystal Structure Analysis. The intensity data of 2642 reflections $F_o>3\sigma(F_o)$, were measured on an automatic Rigaku AFC-5 four-circle diffractometer, three standard reflections after every 100 reflections, employing graphite monochromatized Cu$K\alpha$ radiation (λ=1.5417 Å). The crystals, $C_6H_6O_4Cl_4$, were triclinic, space group P1, Z=3, a=9.623(14) Å, b=10.462(25) Å, c=8.664(14) Å; α=96.48(19), β=88.22(17), and γ=64.71(17)°; V=780.51 Å^3, D_x=1.802 g cm^{-3}. The structure was solved by the direct method, MULTAN 80 (UNICS III System),[4] and the result was refined by the block-diagonal least squares procedure using 2010 non-zero unique reflections with 3°<2θ<120°. The non-H atoms were assigned anisotropic temperature factors. There were three independent molecules (A, B, and C) of essentially the same structure and 17 of the 18 hydrogen atoms could be located on a difference Fourier map and their coordinates were refined with the equivalent isotropic temperature factors of the bonded carbon atoms. The final R value was 0.0930. The atomic scattering factors were obtained from the International Tables for X-ray Crystallography.[5] All calculations were carried out at the Computer Centre of the University of Tokyo.[6]

Discussion

The X-ray crystal structure analysis results show that the compound **A** is the *trans-trans meso*-stereoisomer of 4,4′,5,5′-tetrachloro-2,2′-bi-1,3-dioxolane (**Ia**) and that there are three independent mole-

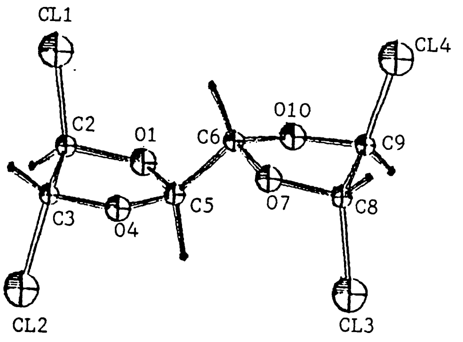


Fig. 1. ORTEP drawing of **Ia** with atomic numbering.

Table 1. Selected Bond Lengths of **Ia** with e.s.d. in Parentheses

Bond	A		B		C		Average	
	l/Å	(e.s.d.)	l/Å	(e.s.d.)	l/Å	(e.s.d.)	l/Å	(e.s.d.)
Cl 1-C 2	1.838	(20)	1.761	(25)	1.769	(27)	1.789	(24)
Cl 2-C 3	1.791	(25)	1.819	(26)	1.676	(24)	1.762	(25)
Cl 3-C 8	1.782	(22)	1.816	(25)	1.638	(29)	1.745	(25)
Cl 4-C 9	1.856	(23)	1.765	(24)	1.844	(22)	1.822	(23)
O 1-C 2	1.387	(26)	1.345	(37)	1.357	(32)	1.363	(32)
O 1-C 5	1.473	(42)	1.431	(25)	1.516	(44)	1.473	(37)
O 4-C 3	1.454	(39)	1.412	(33)	1.460	(35)	1.442	(36)
O 4-C 5	1.467	(28)	1.407	(36)	1.415	(28)	1.430	(31)
O 7-C 6	1.366	(34)	1.415	(25)	1.394	(34)	1.392	(31)
O 7-C 8	1.457	(26)	1.414	(38)	1.418	(34)	1.430	(33)
O 10-C 6	1.467	(26)	1.478	(36)	1.444	(26)	1.463	(29)
O 10-C 9	1.430	(35)	1.351	(31)	1.381	(33)	1.387	(33)
C 2-C 3	1.516	(40)	1.532	(42)	1.619	(45)	1.556	(42)
C 5-C 6	1.546	(32)	1.530	(31)	1.554	(34)	1.543	(32)
C 8-C 9	1.409	(39)	1.562	(40)	1.600	(46)	1.524	(42)

Table 2. Selected Bond Angles of **Ia** with e.s.d in Parentheses

Angle	A		B		C		Average	
	$\phi/^\circ$	(e.s.d.)	$\phi/^\circ$	(e.s.d.)	$\phi/^\circ$	(e.s.d.)	$\phi/^\circ$	(e.s.d.)
C 2-O 1-C 5	105.2	(1.9)	108.1	(1.9)	111.2	(2.3)	108.2	(2.0)
C 3-O 4-C 5	107.0	(2.2)	108.1	(1.9)	110.0	(2.1)	108.4	(2.1)
C 6-O 7-C 8	104.5	(1.7)	109.9	(1.9)	112.0	(2.0)	108.8	(1.9)
C 6-O 10-C 9	102.6	(1.9)	110.4	(1.8)	105.9	(1.9)	106.3	(1.9)
Cl 1-C 2-O 1	111.8	(1.5)	113.9	(2.0)	112.5	(1.8)	112.7	(1.8)
Cl 1-C 2-C 3	107.5	(1.4)	109.2	(1.7)	113.7	(1.6)	110.1	(1.6)
O 1-C 2-C 3	109.5	(2.2)	103.5	(2.1)	102.9	(2.6)	105.3	(2.3)
Cl 2-C 3-O 4	112.3	(1.8)	110.8	(1.7)	118.2	(1.8)	113.8	(1.8)
Cl 2-C 3-C 2	107.3	(1.7)	109.7	(1.5)	110.0	(1.8)	109.0	(1.7)
O 4-C 3-C 2	99.5	(2.0)	101.0	(2.5)	94.6	(2.0)	98.4	(2.2)
O 1-C 5-O 4	107.0	(2.1)	106.3	(2.0)	100.4	(2.1)	104.6	(2.1)
O 1-C 5-C 6	109.0	(2.1)	109.2	(1.5)	108.8	(2.2)	109.0	(1.9)
O 4-C 5-C 6	104.1	(1.8)	110.8	(2.0)	100.7	(1.7)	105.2	(1.8)
O 7-C 6-C 5	110.5	(2.1)	105.3	(1.5)	110.0	(2.1)	108.6	(1.9)
O 7-C 6-O 10	111.7	(1.8)	103.7	(2.0)	106.8	(1.8)	107.4	(1.9)
O 10-C 6-C 5	107.4	(1.7)	107.5	(2.0)	108.3	(1.7)	107.7	(1.8)
Cl 3-C 8-O 7	110.8	(1.5)	110.7	(2.0)	120.8	(2.0)	114.1	(1.8)
Cl 3-C 8-C 9	107.7	(1.5)	108.5	(1.7)	108.1	(1.7)	108.1	(1.6)
O 7-C 8-C 9	106.7	(2.2)	100.3	(1.9)	95.3	(2.5)	100.8	(2.2)
O 10-C 9-C 8	106.9	(1.9)	104.4	(2.4)	105.8	(1.9)	105.7	(2.1)
Cl 4-C 9-O 10	103.4	(1.6)	114.3	(1.7)	107.9	(1.6)	108.5	(1.6)
Cl 4-C 9-C 8	111.1	(1.7)	107.2	(1.4)	114.3	(1.7)	110.9	(1.6)

cules which have essentially the same structure as shown in an ORTEP drawing of the molecule in Fig. 1. Selected bond lengths and bond angles of these three molecules **Ia** are shown in Tables 1 and 2, respectively. The conformation of the molecule is similar to that of 2,2′-bi-1,3-dioxolane.[7] The ^{1}H NMR spectrum of **Ia** (recorded at 500 MHz) shows three sharp singlets of relative intensities 1 : 1 : 1 at δ=5.69 (C2 proton), 6.30, and 6.37 (C4 and C5 protons). The non-interaction between the diastereotopic protons at C4 and C5 of **Ia**, in solution, could possibly be accounted for by the dihedral angle, H4-C4-C5-H5, of nearly 90° estimated from the atomic coordinates. This observation suggests strongly that the conformation of the molecule is essentially the same both in the liquid and the crystalline state.

The authors wish to thank Professor K. F. Mok for helpful discussions.

References

1) L. A. Cort, *J. Chem. Soc.*, **1960**, 3167.

2) H. H. Huang, *J. Chem. Soc.*, **1971**, 1024.

30 B. Fuchs and S. Hauptmann, *Chem. Comm.*, **1971**, 705.

40 T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res. (Jpn.)*, **55**, 69 (1979).

5) "International Tables for X-ray Crystallography," Kynoch Press, Birmingham (1974), Vol. 4.

6) Lists of fractional atomic coordinates, thermal parameters, structure factors and molecular dimensional tables of the three molecules and the structure factors are deposited as Document No. 8923 at the Office of the Editor of Bull. Chem. Soc. Jpn.

7) S. Furberg and O. Hassel, *Acta Chem. Scand.*, **4**, 1584 (1950).