ACTA CHEMICA SCANDINAVICA 24 (1970) 1894–1902

The Crystal Structure of 1,2,3,4,4a,5,6,8a-Octahydro-3,5-bisbromomethyl-3,5-dihydroxy-2,6-dioxo-1,4-ethenonaphthalene

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The crystal structure of a dimeric spiroepoxiketone containing dioxan of crystallisation has been solved using Patterson methods. The compound crystallizes with space group $P2_1/a$ with four formula units in the elementary cell which has the dimensions $a=6.452$ Å, $b=22.154$ Å, $c=12.584$ Å, $\beta=112.46$.

In the oxidation of salicyl alcohol with periodate, a dimeric spiroepoxiketone is formed whose structure, apart from the configuration at the tertiary carbon atoms of the epoxide groups, is known.[1] Since a bisbromohydrin was prepared in the course of the investigation of the dimer, it seemed profitable to determine the structure of the former compound by means of single crystal X-ray methods to determine its full structure.

CRYSTAL DATA

The crystals of 1,2,3,4,4a,5,6,8a-octahydro-3,5-bisbromomethyl-3,5-dihydroxy-2,6-dioxo-1,4-ethenonaphthalene ("dibromide"), containing dioxan of crystallisation, are monoclinic, and since reflexions of the type

$$h0l: l = 2n+1$$
$$0k0: k = 2n+1$$

are absent, they must belong to space group No. 14, $P2_1/c$. The preliminary cell dimensions obtained from Weissenberg films were refined from Guinier powder data, recorded with Cu$K\alpha_1$ radiation ($\lambda=1.54050$ Å) and with lead nitrate ($a=7.8564$ Å) as an internal standard, using the program POWDER.[2] The following values were obtained: $a=6.452\pm0.001$ Å, $b=22.154\pm0.011$ Å, $c=12.584\pm0.007$ Å, $\beta=112.46\pm0.03°$.

The experimental density, $\varrho_{obs} = 1.70$ g cm^{-3}, corresponds to a unit cell content of four formula units, while the calculated density based on $Z = 4$ is 1.74 g cm^{-3}.

The thin platy crystals decomposed readily into "dibromide" and dioxan and, despite mounting in glass capillaries, they did not normally hold for

Table 1. Peaks in the three-dimensional Patterson synthesis, P(*uvw*), ascribable to Br—Br and Br—light atom vectors.

Atom$_1$—atom$_2$	Vector	Peak height	*u*	*v*	*w*
		1000	0	0	0
Br—Br	$2x_1\ 2y_1\ 2z_1$	85	0.488	0.040	0.410
»	$x_1+x_2,\ y_1+y_2,\ z_1+z_2$	160	0.387	0.095	0.468
»	$0,\ \frac{1}{2}-2y_2,\ \frac{1}{2}$	120	0.000	0.260	0.500
»	$x_1-x_2,\ y_2-y_1,\ z_2-z_1$	210	0.150	0.147	0.142
»	$2x_2,\ 2y_2,\ 2z_2$	70	0.210	0.240	0.290
»	$x_1+x_2,\ \frac{1}{2}-(y_1+y_2),(z_1+z_2)$	161	0.365	0.358	0.000
»	$0,\ \frac{1}{2}-2y_1,\ \frac{1}{2}$	170	0.000	0.460	0.500
»	$2x_1,\ \frac{1}{2},\ \frac{1}{2}+2z_1$	184	0.500	0.500	0.095
Br—light atom		100	0.305	0.435	0.260

Table 2. Atomic parameters with their standard deviations and isotropic temperature coefficients.

Atom	*x*	*y*	*z*	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	*B* Å^2
Br(1)	0.2564	0.9778	0.3038	0.0006	0.0002	0.0003	5.38
Br(2)	0.1061	0.1212	0.1437	0.0006	0.0002	0.0003	5.62
C(1)	0.0477	0.2289	0.4914	0.0050	0.0017	0.0027	3.56
C(2)	0.1655	0.8618	0.3942	0.0036	0.0012	0.0026	1.36
C(3)	0.3333	0.4623	0.4354	0.0069	0.0022	0.0036	6.35
C(4)	0.0361	0.8996	0.4366	0.0042	0.0014	0.0023	1.73
C(5)	0.2707	0.8063	0.4692	0.0036	0.0011	0.0019	0.30
C(6)	0.1322	0.5799	0.0545	0.0050	0.0016	0.0028	3.80
C(7)	0.2286	0.6988	0.5058	0.0053	0.0016	0.0026	3.45
C(8)	0.0947	0.8540	0.0175	0.0062	0.0020	0.0033	5.19
C(9)	0.3094	0.7218	0.1658	0.0058	0.0019	0.0030	4.66
C(10)	0.0511	0.7188	0.1262	0.0061	0.0020	0.0032	6.15
C(12)	0.3231	0.6118	0.1252	0.0063	0.0020	0.0035	5.34
C(13)	0.3605	0.5118	0.3833	0.0061	0.0019	0.0033	4.47
C(14)	0.3568	0.9043	0.3855	0.0047	0.0016	0.0026	3.08
C(15)	0.0915	0.7538	0.4523	0.0043	0.0015	0.0024	2.76
C(16)	0.3671	0.7846	0.1345	0.0051	0.0017	0.0027	3.29
C(17)	0.3825	0.6742	0.1009	0.0043	0.0016	0.0023	3.11
O(1)	0.0249	0.8449	0.2764	0.0028	0.0010	0.0015	2.63
O(2)	0.4643	0.3117	0.3006	0.0038	0.0012	0.0019	4.41
O(3)	0.1575	0.4163	0.1145	0.0036	0.0012	0.0019	4.98
O(4)	0.4804	0.5604	0.4666	0.0042	0.0014	0.0023	6.35
O(5)	0.3825	0.6860	0.4480	0.0034	0.0011	0.0018	3.84

Table 3. Calculated and observed structure factors. The columns given are h, k, l, F_o and F_c.

0	2	0	14.4	26.4	0	4	5	16.9	-20.8	1	1	2	46.8	-38.1	1	0	-6	115.2	-122.1
0	4	0	96.6	-95.5	0	5	5	99.7	-104.5	1	1	2	41.4	-38.1	1	0	6	115.2	126.6
0	6	0	40.7	46.2	0	3	5	96.3	-104.5	1	2	2	43.6	46.1	1	0	6	122.5	126.6
0	8	0	88.3	86.1	0	2	5	94.2	93.1	1	2	2	48.0	46.1	1	1	6	14.2	12.9
0	10	0	60.4	67.8	0	2	5	93.6	93.1	1	3	2	91.7	-97.7	1	2	6	12.7	23.6
0	12	0	52.8	-52.8	0	1	5	48.0	-51.0	1	3	2	83.0	-97.7	1	3	6	26.2	21.7
0	14	0	35.1	-33.2	0	3	-6	42.0	-47.5	1	4	2	161.8	155.5	1	5	6	22.3	23.4
0	16	0	38.2	-28.7	0	0	-6	63.6	64.0	1	4	2	178.8	155.5	1	8	6	45.4	42.0
0	20	0	51.7	-36.0	0	0	6	62.6	64.0	1	5	2	13.7	-10.5	1	12	6	45.6	-36.6
0	4	-1	42.8	-42.5	0	1	6	58.7	47.5	1	6	2	93.6	92.4	1	14	-7	46.3	44.6
0	3	-1	28.1	-35.1	0	5	6	60.8	-47.8	1	9	2	115.6	-111.0	1	9	-7	41.1	26.4
0	17	1	34.9	33.5	0	7	6	85.0	-87.1	1	11	2	70.0	-69.7	1	8	-7	47.6	50.6
0	16	1	59.9	58.7	0	8	6	50.7	39.3	1	12	2	43.8	36.5	1	7	-7	55.3	54.0
0	15	1	48.2	46.6	0	10	6	29.2	17.9	1	16	2	36.8	-30.2	1	6	-7	58.8	64.9
0	14	1	90.0	89.5	0	12	6	33.8	-46.2	1	18	2	42.8	-45.2	1	5	-7	13.7	-7.0
0	13	1	67.0	-56.7	0	13	6	45.0	-42.4	1	13	-3	45.1	27.7	1	4	-7	15.9	12.3
0	12	1	68.9	65.6	0	5	-7	61.5	-25.4	1	12	-3	53.1	52.3	1	3	-7	24.9	-16.8
0	11	1	35.5	-36.7	0	1	-7	72.2	85.5	1	10	-3	154.0	148.0	1	1	-7	83.6	109.5
0	9	1	26.5	-20.7	0	1	7	72.2	85.5	1	8	-3	34.2	45.2	1	1	-7	92.0	109.5
0	8	1	98.1	105.4	0	5	7	61.5	-25.4	1	6	-3	42.8	-34.0	1	1	7	14.4	5.1
0	7	1	44.2	49.6	0	7	7	31.0	59.8	1	5	-3	36.9	25.3	1	2	7	21.6	-16.3
0	6	1	129.3	137.1	0	8	7	35.6	41.4	1	5	-3	33.8	23.3	1	3	7	59.1	-72.7
0	4	1	42.8	42.5	0	9	7	51.4	30.3	1	3	-3	66.0	-78.8	1	3	7	57.5	-72.7
0	4	1	45.0	42.5	0	12	7	42.2	46.5	1	3	-3	77.5	-78.8	1	4	7	21.8	22.2
0	3	1	28.1	-35.1	0	5	-8	28.4	-32.5	1	2	-3	150.1	124.6	1	5	7	50.8	-62.2
0	3	1	33.7	-35.1	0	4	-8	50.7	-64.7	1	2	-3	147.9	124.6	1	5	7	63.2	-62.2
0	5	-2	40.9	-32.3	0	2	-8	25.2	-63.8	1	1	-3	197.7	-149.2	1	6	7	56.1	58.5
0	4	-2	36.3	-32.5	0	1	-8	14.1	14.4	1	1	-3	156.9	-149.2	1	0	-8	70.1	82.3
0	3	-2	191.2	200.0	0	1	8	14.1	-14.4	1	2	3	109.8	97.7	1	0	-8	78.8	82.3
0	2	-2	110.5	-98.3	0	2	8	32.6	-40.8	1	2	3	93.0	97.7	1	1	-8	12.6	-17.5
0	1	-2	80.0	71.8	0	2	8	25.2	-40.8	1	3	3	97.5	99.6	1	4	-8	32.2	-29.0
0	0	-2	27.8	17.0	0	4	8	50.7	-64.7	1	3	3	80.6	89.6	1	4	-8	34.0	-29.0
0	19	2	36.3	-11.2	0	6	8	60.8	-64.7	1	5	3	139.3	123.1	1	5	-8	23.4	-27.7
0	17	2	63.2	-49.2	0	5	8	28.4	32.5	1	5	3	126.0	123.1	1	7	-8	46.3	-52.6
0	15	2	37.5	-37.7	0	2	-9	35.1	45.7	1	6	3	27.2	31.5	1	8	-8	43.2	48.9
0	12	2	32.6	18.5	0	1	-9	16.5	-27.4	1	8	3	49.9	49.9	1	12	-8	50.5	-45.1
0	11	2	87.1	-80.7	0	10	9	51.9	-51.7	1	9	3	73.8	-61.3	1	5	8	16.9	-20.7
0	9	2	84.5	-91.6	0	2	9	45.6	-45.7	1	10	3	54.6	59.3	1	3	8	33.7	-31.3
0	8	2	72.8	-77.1	0	1	9	16.5	-27.4	1	11	3	52.4	47.1	1	2	8	23.3	-30.9
0	7	2	57.6	48.3	0	4	-10	23.7	37.8	1	12	3	59.7	65.8	1	5	-9	25.3	-35.6
0	6	2	90.5	-91.8	0	2	-10	15.4	24.3	1	13	3	37.0	39.7	1	3	-9	35.6	-55.4
0	5	2	35.5	37.9	0	1	-10	15.8	12.8	1	17	3	59.8	-46.1	1	3	-9	47.5	-55.4
0	5	2	40.9	37.9	0	1	10	15.8	12.8	1	16	-4	64.5	-71.6	1	2	-9	22.5	27.3
0	4	2	36.9	-32.5	0	2	10	15.4	24.3	1	12	-4	75.5	73.2	1	2	9	14.5	-15.7
0	4	2	30.4	-32.5	0	1	10	15.8	-12.8	1	6	-4	122.8	96.1	1	5	-10	24.5	-20.0
0	3	2	191.2	-200.0	0	2	-11	15.9	-28.0	1	5	-4	29.5	20.8	1	3	-10	31.7	39.1
0	3	2	208.0	-200.0	0	2	11	15.9	28.0	1	5	-4	26.9	20.8	1	5	-11	24.8	42.3
0	2	2	110.5	-98.3	0	1	11	16.0	28.0	1	4	-4	149.2	139.1	2	0	0	46.8	-45.8
0	2	2	98.0	-98.3	1	1	0	147.1	115.1	1	4	-4	133.6	139.1	2	1	0	113.1	-89.8
0	1	2	80.0	-71.8	1	2	0	42.8	-36.1	1	3	-4	29.0	26.6	2	1	0	81.9	-89.8
0	1	2	72.4	-71.8	1	2	0	33.5	-36.1	1	3	-4	24.8	26.6	2	2	0	120.4	-105.5
0	0	2	29.1	17.0	1	3	0	90.0	-96.2	1	2	-4	112.7	99.3	2	3	0	80.3	-67.7
0	5	-3	111.0	104.9	1	3	0	99.9	-96.2	1	2	-4	96.2	99.3	2	3	0	62.0	-67.7
0	4	-3	26.9	-23.3	1	4	0	136.5	-129.5	1	1	-4	34.3	-34.9	2	4	0	112.0	-102.1
0	3	-3	109.1	111.8	1	4	0	145.7	-129.5	1	1	-4	36.4	-34.9	2	5	0	40.8	35.2
0	2	-3	97.3	76.1	1	5	0	75.1	77.7	1	0	4	58.8	-53.2	2	5	0	40.2	35.2
0	1	-3	83.8	76.2	1	5	0	76.0	77.7	1	0	4	44.8	-53.2	2	6	0	61.6	-57.9
0	18	3	42.7	-36.9	1	6	0	70.2	-81.7	1	1	4	83.4	78.1	2	7	0	51.1	50.0
0	17	3	59.0	-56.4	1	7	0	140.1	132.3	1	1	4	91.0	78.1	2	8	0	21.1	-17.1
0	13	3	42.4	40.2	1	8	0	138.7	136.8	1	2	4	119.3	-115.1	2	10	0	33.9	-37.9
0	12	3	40.4	-38.2	1	9	0	26.3	32.7	1	2	4	105.6	-115.1	2	11	0	78.3	-72.8
0	10	3	36.5	-36.1	1	10	0	28.1	-25.0	1	3	4	60.6	56.2	2	15	0	33.7	33.4
0	9	3	41.3	-57.2	1	11	0	59.9	54.6	1	4	4	99.2	96.2	2	16	0	22.7	29.7
0	8	3	71.8	-65.1	1	12	0	51.8	-54.7	1	5	4	45.1	-43.6	2	18	0	44.0	38.5
0	6	3	74.9	-78.1	1	13	0	79.8	68.6	1	5	4	42.5	-43.6	2	19	0	44.5	-40.7
0	5	3	111.0	104.9	1	15	0	68.2	63.9	1	8	4	29.6	-26.9	2	20	0	28.9	18.5
0	5	3	112.7	104.9	1	16	-1	42.0	-39.7	1	12	-5	51.6	-55.0	2	1	-1	140.5	135.1
0	4	3	20.7	23.3	1	13	-1	79.5	-71.4	1	10	-5	67.3	-77.6	2	2	-1	26.4	-30.0
0	4	3	26.9	23.3	1	11	-1	42.1	-40.9	1	8	-5	37.4	45.2	2	2	-1	19.7	-30.0
0	3	3	103.0	111.8	1	9	-1	87.8	90.1	1	7	-5	38.6	-29.1	2	3	-1	64.6	-63.0
0	3	3	119.1	111.8	1	8	-1	63.1	-62.5	1	6	-5	31.2	-31.2	2	4	-1	107.2	85.0
0	2	3	91.4	-76.1	1	7	-1	105.7	108.5	1	5	-5	20.0	31.7	2	5	-1	27.6	-30.0
0	2	3	87.5	-76.1	1	6	-1	31.7	-33.0	1	5	-5	27.6	31.7	2	5	-1	27.2	-30.0
0	1	3	82.0	76.2	1	5	-1	85.2	93.0	1	4	-5	23.1	-32.6	2	6	-1	49.2	44.2
0	1	3	83.8	76.2	1	4	-1	43.0	-47.5	1	4	-5	29.7	-32.6	2	7	-1	89.8	89.6
0	0	-4	89.6	-88.0	1	4	-1	49.6	-47.5	1	3	-5	55.7	47.7	2	8	-1	52.8	62.3
0	1	-4	93.8	18.0	1	3	-1	16.3	23.4	1	3	-5	52.2	47.7	2	9	-1	26.0	23.4
0	2	-4	24.2	-18.9	1	2	-1	36.1	-44.6	1	2	-5	91.1	-94.4	2	10	-1	36.1	37.0
0	3	-4	108.5	-98.1	1	2	-1	41.5	-44.6	1	2	-5	93.8	-94.4	2	11	-1	22.9	-23.5
0	4	-4	107.1	136.7	1	1	-1	129.9	97.9	1	1	-5	50.9	-58.1	2	12	-1	57.5	44.9
0	16	4	38.1	-16.0	1	1	1	136.5	-159.8	1	1	-5	55.1	-58.1	2	13	-1	60.6	-56.9
0	15	4	40.3	38.7	1	1	1	169.0	-159.8	1	1	5	30.7	32.8	2	14	-1	69.5	57.6
0	13	4	43.7	28.7	1	2	1	121.4	-123.5	1	1	5	25.6	32.8	2	15	-1	28.1	29.7
0	12	4	55.4	49.3	1	2	1	138.8	-123.5	1	2	5	103.9	87.7	2	16	-1	29.1	29.7
0	11	4	47.7	58.8	1	3	1	100.6	-91.5	1	2	5	90.8	87.7	2	17	-1	35.9	32.8
0	10	4	46.5	-41.4	1	3	1	82.5	-91.5	1	3	5	28.0	19.5	2	19	-1	24.2	-27.5
0	9	4	115.3	114.5	1	4	1	41.8	-39.9	1	3	5	31.4	19.5	2	2	1	54.5	-61.1
0	8	4	101.2	-95.1	1	4	1	45.6	-39.9	1	4	5	46.4	-49.6	2	2	1	59.3	-61.1
0	7	4	47.8	39.1	1	5	1	82.9	-78.5	1	4	5	49.1	-49.6	2	3	1	94.7	85.6
0	6	4	55.9	54.8	1	5	1	86.9	-78.5	1	5	5	23.9	-29.1	2	3	1	87.6	85.6
0	4	4	112.4	106.7	1	6	1	53.5	51.7	1	5	5	35.5	-29.1	2	4	1	71.7	-67.7
0	4	4	107.1	106.7	1	10	1	126.6	-110.1	1	6	5	112.0	-126.2	2	4	1	77.6	-67.7
0	3	4	100.1	95.1	1	12	1	59.6	-55.7	1	7	5	40.7	21.4	2	5	1	24.0	21.9
0	3	4	109.5	95.1	1	14	1	46.7	45.5	1	8	5	45.7	-40.9	2	5	1	29.1	21.9
0	2	4	24.5	-18.9	1	15	-2	81.6	-86.9	1	9	5	34.5	26.3	2	6	1	16.8	-8.7
0	2	4	24.2	-18.9	1	13	-2	57.0	-63.5	1	14	5	54.1	-58.7	2	7	1	42.4	-40.7
0	1	4	24.2	-18.9	1	9	-2	63.5	-61.0	1	13	-6	39.9	38.7	2	8	1	37.7	-34.4
0	1	4	22.8	-18.9	1	8	-2	29.7	31.8	1	7	-6	85.0	71.3	2	9	1	38.9	-36.5
0	0	4	98.7	-98.9	1	7	-2	121.4	-115.0	1	6	-6	79.1	-76.9	2	10	1	109.3	-106.1
0	1	-5	48.3	-53.9	1	6	-2	171.5	-178.4	1	5	-6	63.9	68.3	2	11	1	34.2	27.6
0	2	-5	93.6	-93.1	1	5	-2	172.1	-163.7	1	5	-6	61.8	68.3	2	12	1	55.6	-50.7
0	3	-5	98.3	-134.5	1	5	-2	174.0	-163.7	1	4	-6	47.8	-51.9	2	13	1	31.7	24.5
0	4	-5	10.8	33.6	1	4	-2	93.3	-94.0	1	4	-6	59.7	-51.9	2	16	1	29.9	-26.4
0	5	-5	42.2	-39.5	1	4	-2	109.9	-96.9	1	3	-6	64.5	-71.6	2	17	1	29.2	-31.9
0	11	5	33.6	26.5	1	3	-2	91.1	93.6	1	3	-6	76.4	-71.6	2	18	1	45.3	-44.5
0	10	5	91.6	76.6	1	3	-2	90.4	93.6	1	2	-6	93.4	-98.4	2	20	-2	44.6	-38.0
0	9	5	44.1	-30.4	1	2	-2	139.6	-142.1	1	2	-6	37.8	-38.4	2	17	-2	27.7	-21.8
0	7	5	43.4	-43.6	1	2	-2	147.1	-142.1	1	1	-6	40.7	-36.0	2	15	-2	33.6	-29.7
0	6	5	79.6	-87.6	1	1	-2	151.9	147.4	1	1	-6	40.9	-36.0	2	14	-2	24.6	-24.6
0	5	5	82.2	-73.5	1	1	-2	153.6	147.4	1	0	-6	123.6	-122.1	2	13	-2	39.3	-39.5

Table 3. Continued.

2	12	-2	37.1	-37.5	2	1	-5	41.2	39.0	3	4	0	49.3	48.4	3	3	3	35.8	-35.4
2	11	-2	19.7	-19.6	2	1	5	45.6	43.3	3	4	0	47.8	48.4	3	4	3	17.2	-14.1
2	10	-2	27.1	33.6	2	1	-6	67.9	73.1	3	5	0	13.9	-7.1	3	6	3	74.7	-67.2
2	9	-2	15.5	14.2	2	2	6	30.6	34.8	3	6	0	24.8	27.0	3	8	3	41.5	-48.3
2	8	-2	81.6	99.3	2	2	5	36.2	36.9	3	7	0	17.1	-11.6	3	9	3	21.3	-23.0
2	7	-2	116.4	-110.8	2	3	5	28.2	34.5	3	9	0	66.5	-58.9	3	12	3	21.0	-8.9
2	6	-2	31.4	-31.6	2	6	5	35.2	-23.2	3	10	0	25.7	15.3	3	14	3	56.3	-51.1
2	5	-2	27.6	-28.5	2	7	5	50.7	44.2	3	11	0	101.0	-98.6	3	16	3	33.7	-29.2
2	4	-2	77.4	-78.5	2	9	5	37.5	41.0	3	12	0	14.7	12.3	3	24	-4	15.6	6.6
2	2	-2	211.7	173.6	2	10	5	34.3	40.0	3	13	0	21.3	-6.6	3	22	-4	19.9	14.9
2	0	-2	195.6	194.2	2	13	5	37.7	-38.4	3	14	0	24.1	-17.4	3	15	-4	29.3	-31.8
2	0	2	74.8	-85.3	2	17	-6	26.5	-33.1	3	16	0	30.3	-32.0	3	14	-4	26.0	29.0
2	1	2	14.5	7.9	2	11	-6	76.4	-72.1	3	17	0	34.6	-19.3	3	13	-4	25.9	-22.4
2	2	2	32.2	32.7	2	10	-6	21.9	-23.5	3	18	0	21.9	17.0	3	10	-4	28.0	-26.0
2	2	2	32.5	32.7	2	9	-6	59.6	-70.3	3	19	0	36.4	-22.3	3	8	-4	22.8	-36.5
2	3	2	21.6	21.5	2	8	-6	62.6	-65.4	3	1	-1	67.1	-50.9	3	7	-4	66.1	-94.7
2	4	2	21.4	21.5	2	7	-6	16.4	-0.4	3	2	-1	46.8	-48.6	3	5	-4	70.1	-63.5
2	4	2	162.7	136.4	2	6	-6	15.9	16.1	3	3	-1	76.1	-67.0	3	4	-4	105.1	-88.4
2	5	2	34.5	38.4	2	5	-6	23.7	-17.5	3	4	-1	23.7	-24.7	3	3	-4	58.1	63.2
2	5	2	29.9	38.4	2	5	-6	22.2	-17.5	3	4	-1	19.7	-24.7	3	2	-4	73.4	-69.4
2	7	2	30.0	23.0	2	3	-6	34.7	-35.4	3	5	-1	97.6	-93.4	3	1	-4	11.9	20.3
2	9	2	50.9	46.5	2	3	-6	30.9	-36.4	3	5	-1	100.1	-93.4	3	1	-4	14.5	20.3
2	10	2	46.7	-43.6	2	2	-6	27.4	-32.4	3	6	-1	91.5	97.7	3	0	-4	104.7	-89.7
2	11	2	30.3	32.9	2	2	-6	26.1	-32.4	3	7	-1	16.0	1.9	4	0	4	68.9	70.8
2	12	2	34.5	30.8	2	1	-6	36.8	-44.8	3	8	-1	22.3	22.0	4	0	4	87.5	70.8
2	13	2	24.3	20.3	2	1	-6	36.6	-44.8	3	10	-1	32.7	-23.4	3	1	4	16.1	5.6
2	15	2	35.3	31.6	2	0	-6	60.4	-61.9	3	11	-1	22.4	-26.6	3	2	4	48.1	42.5
2	16	2	47.1	-43.5	2	0	-6	67.7	-61.9	3	14	-1	33.5	21.5	3	2	4	37.2	42.5
2	17	2	28.6	22.7	2	0	6	21.5	-0.1	3	15	-1	24.5	22.8	3	3	4	37.4	34.6
2	17	-3	33.1	37.4	2	1	6	16.9	-17.6	3	17	-1	28.1	14.7	3	3	4	35.0	34.6
2	16	-3	22.7	-10.1	2	1	6	21.6	-17.6	3	1	1	12.0	16.1	3	4	4	18.9	-7.5
2	15	-3	26.0	25.3	2	4	6	43.0	-41.8	3	1	1	16.1	16.1	3	5	4	42.0	-27.8
2	14	-3	64.6	-48.0	2	4	6	48.0	-41.8	3	2	1	17.8	-19.5	3	5	4	27.2	-27.8
2	12	-3	51.8	-50.5	2	6	6	44.5	-42.5	3	2	1	12.8	-19.5	3	6	4	19.6	13.6
2	11	-3	32.9	-23.3	2	7	6	59.3	57.2	3	3	1	105.4	105.6	3	7	4	23.7	-16.4
2	10	-3	33.9	45.0	2	8	6	39.1	41.1	3	3	1	125.1	105.6	3	8	4	68.3	56.3
2	9	-3	53.6	-46.6	2	16	-7	28.9	30.7	3	4	1	13.6	12.9	3	9	4	32.0	34.7
2	8	-3	20.9	-11.9	2	14	-7	33.6	42.2	3	5	1	114.1	103.4	3	12	4	21.7	-14.6
2	7	-3	30.4	30.3	2	12	-7	22.7	15.1	3	6	1	95.4	91.8	3	15	4	23.7	-13.5
2	6	-3	73.2	-84.9	2	10	-7	25.5	-27.1	3	8	1	59.9	40.4	3	18	4	24.1	-14.4
2	5	-3	48.6	-39.3	2	8	-7	34.0	37.5	3	9	1	44.4	-37.3	3	20	4	23.6	-13.0
2	5	-3	40.2	-39.3	2	7	-7	23.4	-28.6	3	10	1	19.5	10.7	3	18	-5	21.9	29.1
2	4	-3	67.9	-68.4	2	6	-7	59.0	74.3	3	11	1	37.3	32.4	3	14	-5	17.3	13.4
2	4	-3	79.2	-68.6	2	5	-7	62.7	-69.8	3	13	1	23.9	19.0	3	13	-5	33.3	28.4
2	3	-3	87.7	-76.1	2	5	-7	63.1	-69.8	3	14	1	22.6	18.8	3	12	-5	35.0	43.8
2	2	-3	101.4	100.4	2	4	-7	16.7	19.0	3	15	1	21.3	-8.0	3	11	-5	15.4	14.0
2	1	-3	67.3	-61.5	2	4	-7	19.9	19.9	3	16	1	23.6	12.7	3	10	-5	58.6	72.9
2	1	-3	44.9	-51.5	2	3	-7	55.4	-40.7	3	17	1	47.7	-36.7	3	8	-5	37.5	36.5
2	1	3	112.7	-106.9	2	3	-7	57.1	-40.7	3	19	1	23.5	-25.8	3	6	-5	14.2	5.4
2	1	3	123.7	-106.9	2	2	-7	25.0	-24.2	3	0	-2	85.0	95.6	3	1	-5	78.8	-74.7
2	2	3	25.2	22.3	2	2	-7	21.4	-24.2	3	1	-2	14.0	-14.8	3	1	-5	59.7	-74.7
2	2	3	26.3	22.3	2	2	7	30.2	-26.0	3	2	-2	35.4	25.5	3	2	-5	27.2	30.6
2	4	3	21.5	27.0	2	2	7	27.0	-26.0	3	3	-2	39.7	31.0	3	2	-5	21.6	30.6
2	4	3	27.6	27.0	2	5	7	34.5	-32.1	3	4	-2	12.5	-24.5	3	3	-5	66.6	59.7
2	5	3	37.2	-41.5	2	5	7	25.5	-32.1	3	4	-2	16.4	-24.5	3	5	-5	13.4	10.6
2	5	3	30.7	-41.5	2	7	7	26.2	22.4	3	5	-2	36.5	32.8	3	5	-5	14.2	10.6
2	6	3	63.5	-65.6	2	10	7	40.9	-42.1	3	5	-2	44.0	32.8	3	1	5	18.4	3.1
2	7	3	78.2	-68.9	2	14	7	25.7	14.6	3	6	-2	31.5	27.6	3	2	5	26.2	23.5
2	8	3	24.3	14.4	2	8	-8	61.8	-59.4	3	7	-2	56.9	59.4	3	2	5	19.7	23.5
2	9	3	70.8	-56.0	2	7	-8	55.4	40.8	3	8	-2	56.3	54.8	3	3	5	34.2	-25.5
2	10	3	95.5	89.2	2	6	-8	59.3	49.8	3	9	-2	35.2	27.9	3	4	5	31.6	28.1
2	12	3	25.7	22.0	2	5	-8	24.4	17.5	3	10	-2	38.2	37.7	3	4	5	21.6	28.1
2	13	3	40.9	45.5	2	5	-8	20.5	17.5	3	11	-2	34.1	24.3	3	5	5	37.9	-33.0
2	19	3	29.7	27.1	2	3	-8	18.3	-16.0	3	12	-2	42.8	-33.4	3	5	5	28.7	-33.0
2	19	-4	31.6	36.6	2	2	-8	43.2	41.3	3	13	-2	69.5	68.1	3	6	5	29.5	29.1
2	17	-4	33.5	23.1	2	2	-8	36.3	41.3	3	14	-2	30.4	-30.4	3	8	5	25.4	21.5
2	16	-4	36.1	28.5	2	1	-8	19.6	-27.0	3	15	-2	24.4	18.9	3	9	5	33.3	19.2
2	15	-4	44.8	56.5	2	1	-8	28.6	-27.0	3	16	-2	21.1	18.4	3	13	5	47.5	-32.6
2	12	-4	39.3	42.0	2	0	-8	71.9	82.3	3	20	-2	33.3	-31.5	3	14	5	36.2	28.0
2	11	-4	81.4	92.3	2	0	-8	66.9	82.3	3	0	2	89.6	-81.9	3	19	-6	21.4	-10.0
2	9	-4	54.4	55.7	2	0	8	24.2	-6.0	3	0	2	92.8	-81.9	3	18	-6	25.9	-29.9
2	8	-4	53.4	-61.5	2	1	8	20.3	-29.4	3	1	2	69.4	52.2	3	16	-6	28.2	-33.7
2	6	-4	15.4	-16.4	2	1	8	31.4	-29.4	3	1	2	56.1	52.2	3	13	-6	22.3	-15.5
2	5	-4	41.2	37.1	2	2	8	19.2	25.2	3	2	2	56.1	-44.9	3	11	-6	24.9	-27.8
2	5	-4	43.9	37.1	2	3	8	31.1	-32.4	3	2	2	50.2	-44.9	3	9	-6	16.2	-26.0
2	4	-4	16.4	3.1	2	3	8	37.4	-32.4	3	3	2	60.2	52.9	3	6	-6	26.4	26.4
2	4	-4	15.1	3.1	2	4	8	53.0	57.6	3	4	2	21.8	19.4	3	0	-6	35.1	-38.8
2	3	-4	135.3	135.3	2	5	8	20.1	-16.2	3	4	2	17.9	19.4	3	0	-6	37.8	-38.8
2	3	-4	145.7	135.3	2	7	8	28.9	23.6	3	5	2	17.3	15.4	3	2	-6	78.2	74.5
2	1	-4	81.6	99.9	2	14	-9	26.5	-29.3	3	5	2	18.5	15.4	3	2	-6	81.7	74.5
2	1	-4	93.9	99.9	2	13	-9	28.9	-21.0	3	6	2	16.4	-16.3	3	4	-6	75.7	97.1
2	0	4	19.1	14.0	2	10	-9	30.9	-44.8	3	8	2	59.3	-45.6	3	4	-6	90.2	97.1
2	1	4	62.0	58.6	2	8	-9	46.5	-42.0	3	9	2	73.2	56.1	3	5	-6	42.5	-36.9
2	1	4	76.5	58.6	2	7	-9	27.3	32.2	3	11	2	42.8	33.6	3	1	6	85.4	-80.1
2	2	4	12.7	-9.1	2	6	-9	24.6	-24.2	3	12	2	31.7	28.7	3	2	6	44.7	-40.8
2	2	4	17.7	-9.1	2	5	-9	49.2	-50.3	3	17	2	23.8	13.5	3	3	6	27.8	-22.3
2	3	4	28.5	24.3	2	5	-9	48.6	-50.3	3	19	2	25.2	20.8	3	4	6	21.5	-22.4
2	3	4	32.9	24.3	2	4	-9	21.5	-26.0	3	20	2	26.5	23.8	3	5	6	27.2	19.4
2	4	4	41.7	-35.1	2	4	-9	22.0	-26.0	3	22	2	23.6	16.3	3	5	6	16.4	19.4
2	5	4	36.7	-43.8	2	2	-9	35.9	41.5	3	21	-3	21.0	-18.3	3	6	6	39.9	-27.2
2	7	4	49.4	-46.1	2	2	-9	30.8	41.5	3	19	-3	20.0	-10.6	3	11	6	33.4	-28.7
2	8	4	44.1	38.0	2	1	-9	31.0	34.0	3	16	-3	29.9	-19.9	3	15	-7	20.0	-0.4
2	10	4	25.5	-25.1	2	1	-9	30.6	34.9	3	15	-3	22.4	-17.5	3	10	-7	23.4	-26.6
2	13	4	39.1	-37.6	2	5	-10	39.3	-37.8	3	14	-3	43.2	-45.7	3	13	-7	21.2	35.4
2	15	4	31.3	-29.7	2	5	-10	39.5	-37.8	3	13	-3	31.0	-17.5	3	12	-7	31.9	-37.1
2	17	-5	34.0	-38.1	2	4	-10	24.7	-27.1	3	12	-3	30.4	-16.9	3	10	-7	44.7	-55.3
2	15	-5	38.6	-36.8	2	3	-10	23.4	24.2	3	11	-3	24.7	-20.1	3	9	-7	20.7	-17.7
2	14	-5	26.4	-27.1	2	2	-10	19.1	-32.9	3	10	-3	21.0	-17.1	3	8	-7	21.8	-27.0
2	11	-5	25.5	36.1	2	2	-10	27.7	-32.9	3	9	-3	43.1	62.8	3	5	-7	24.8	-13.1
2	10	-5	37.6	29.8	2	2	-11	33.2	45.4	3	8	-3	20.1	-14.0	3	5	-7	15.4	-13.1
2	9	-5	32.9	-40.5	2	2	-11	40.8	45.4	3	7	-3	40.7	54.3	3	4	-7	55.0	-50.5
2	7	-5	30.0	-31.7	2	10	-11	23.9	27.4	3	6	-3	62.1	-93.3	3	4	-7	57.4	-50.5
2	6	-5	46.1	43.6	2	9	-11	20.7	19.1	3	4	-3	78.8	-82.3	3	3	-7	14.7	-17.2
2	5	-5	159.0	159.2	2	2	-12	15.1	17.7	3	3	-3	71.3	71.3	3	2	-7	53.0	-61.7
2	5	-5	130.8	159.2	3	1	0	24.9	-37.1	3	1	-3	73.1	72.2	3	2	-7	44.7	-61.7
2	4	-5	42.8	-33.8	3	1	0	24.9	-32.1	3	1	3	19.7	-14.7	3	1	-7	52.5	-55.0
2	4	-5	26.4	-32.8	3	2	0	20.4	-19.9	3	1	3	13.8	-16.7	3	1	-7	44.8	-55.0
2	3	-5	123.1	137.0	3	2	0	23.3	-19.9	3	2	3	56.1	40.4	3	5	7	19.1	27.1
2	3	-5	93.7	137.0	3	3	0	54.4	-54.6	3	2	3	45.1	40.4	3	5	7	21.8	27.1
2	1	-5	30.6	30.3	3	3	0	53.6	-54.6	3	3	3	52.7	-39.4	3	10	7	29.8	-23.7

Table 3. Continued.

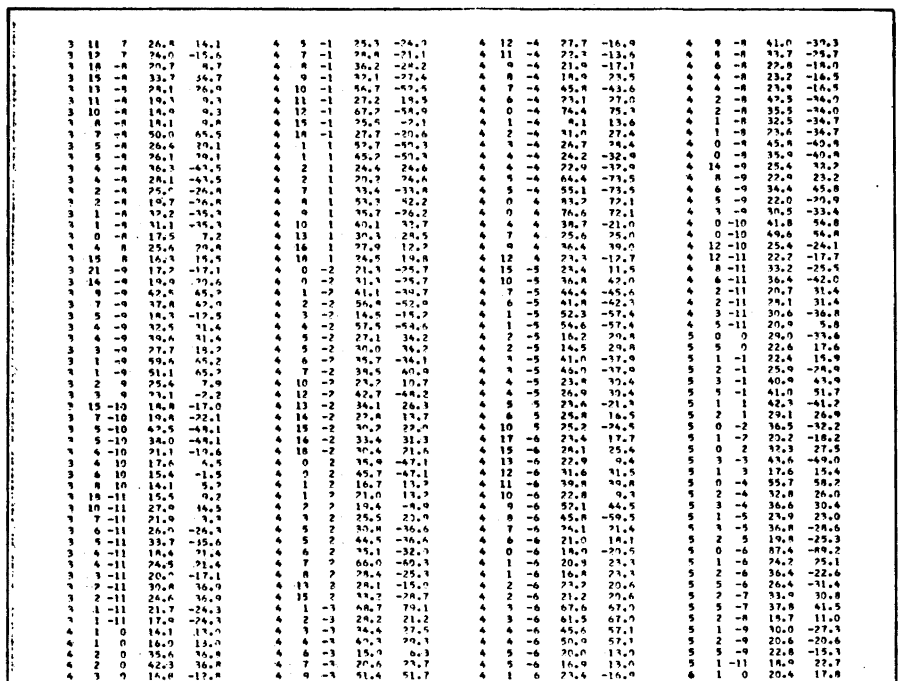

Table 4. Selected interatomic distances with their standard deviations.

Bond	$L \pm \sigma$ Å	Bond	$L \pm \sigma$ Å
C(14)—Br(1)	1.89 ± 0.04	C(7)—C(8)	1.50 ± 0.05
C(8)—Br(2)	2.02 ± 0.04	C(7)—C(15)	1.53 ± 0.05
C(1)—C(10)	1.37 ± 0.05	C(7)—C(16)	1.58 ± 0.04
C(1)—C(15)	1.42 ± 0.04	C(9)—C(10)	1.56 ± 0.05
C(2)—C(4)	1.43 ± 0.04	C(9)—C(16)	1.50 ± 0.06
C(2)—C(5)	1.55 ± 0.03	C(9)—C(17)	1.50 ± 0.05
C(2)—C(14)	1.59 ± 0.04	C(12)—C(17)	1.52 ± 0.06
C(3)—C(13)	1.35 ± 0.06	O(9)—C(2)	1.46 ± 0.02
C(4)—C(6)	1.44 ± 0.04	O(2)—C(16)	1.24 ± 0.04
C(5)—C(17)	1.60 ± 0.04	O(3)—C(4)	1.22 ± 0.03
C(6)—C(12)	1.39 ± 0.05	O(4)—C(3)	1.43 ± 0.05
		O(4)—C(13)	1.50 ± 0.05
		O(5)—C(7)	1.42 ± 0.04

Table 5. Bond angles with their standard deviations.

Angle	$\theta \pm \sigma°$	Angle	$\theta \pm \sigma°$
C(10)–C(9)–C(15)	116.8±2.8	C(16)–C(7)–O(5)	110.5±2.4
C(4)–C(2)–C(5)	114.9±1.6	Br(2)–C(8)–O(7)	106.4±2.4
C(4)–C(2)–C(14)	106.6±2.3	C(10)–C(9)–C(16)	107.8±3.1
C(4)–C(2)–O(1)	108.1±1.8	C(10)–C(9)–C(17)	107.1±3.0
C(5)–C(2)–C(14)	110.3±1.9	C(16)–C(9)–C(17)	111.1±2.8
C(5)–C(2)–O(1)	111.1±2.0	C(1)–C(10)–C(9)	110.0±3.0
C(14)–C(2)–O(1)	105.5±1.5	C(6)–C(12)–C(17)	124.7±3.4
C(13)–C(3)–O(4)	119.2±3.6	C(3)–C(13)–O(4)	111.6±3.3
C(2)–C(4)–C(6)	118.8±2.2	Br(1)–C(14)–O(2)	114.5±1.8
C(2)–C(4)–O(3)	127.1±2.4	C(1)–C(15)–C(5)	110.1±2.6
C(6)–C(4)–O(3)	114.0±2.6	C(1)–C(15)–C(7)	111.1±2.6
C(2)–C(5)–C(15)	112.3±1.9	C(5)–C(15)–C(7)	105.3±2.1
C(2)–C(5)–C(17)	110.1±2.0	C(7)–C(16)–C(9)	112.8±2.8
C(15)–C(5)–C(17)	110.0±2.0	C(7)–C(16)–O(2)	123.1±3.0
C(4)–C(6)–C(12)	115.9±3.1	C(9)–C(16)–O(2)	122.0±3.0
C(8)–C(7)–C(15)	114.2±2.7	C(5)–C(17)–C(9)	105.6±2.5
C(8)–C(7)–C(16)	100.5±2.6	C(5)–C(17)–C(12)	113.5±2.5
C(8)–C(7)–O(5)	115.6±3.0	C(9)–C(17)–C(12)	113.0±2.7
C(15)–C(7)–C(16)	104.5±2.7	C(3)–O(4)–C(13)	111.7±3.1
C(15)–C(7)–O(5)	110.5±2.5		

longer than the time needed to collect data from one or two layers. Crystals were rotated about all three crystallographic axes, and all zones which could be examined with Cu$K\alpha$-radiation were recorded. Some of the Weissenberg data, especially those obtained from rotation about the a-axis were, however, of poor quality and therefore not included in the least squares refinement.

STRUCTURE DETERMINATION

A three-dimensional Patterson synthesis of the visually estimated Weissenberg data showed predominant maxima at the positions indicated in Table 1. Of the nine well-developed peaks with heights >70, eight could be accounted for by assuming that the bromine atoms occupied the following positions:

	x	y	z
Br(1)	0.255	0.980	0.295
Br(2)	0.100	0.120	0.150

From a Fourier synthesis based on these preliminary bromine positions, eleven of the light atoms could be located, and a subsequent Fourier calculation revealed the positions of all remaining atoms with exception for the hydrogen atoms. A structure factor calculation based on the preliminary atomic positions yielded an R-value of 0.25. A full matrix least squares refinement of the structure, based on 1260 independent reflexions, allowing for isotropic temperature coefficients for all atoms, converged to give an R-value of 0.142 which, regarding the rather poor quality of the intensity material,

is a good value. The final atomic parameters and isotropic temperature coefficients are given in Table 2, and observed and calculated structure factors are listed in Table 3.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Selected important interatomic distances and angles with their standard deviations are given in Tables 4 and 5. The structure of one formula unit, showing all bond distances, is pictured in Fig. 1, while the packing of the

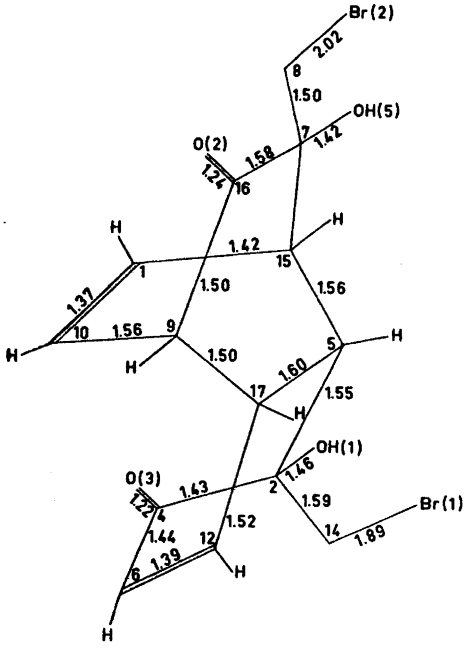

Fig. 1. A formula unit of 1,2,3,4,4a,5,6,8a-octahydro - 3,5 - bisbromomethyl - 3,5 - dihydroxy - 2,6 - dioxo - 1,4 - ethenonaphthalene showing bond distances.

molecules is illustrated in Fig. 2. The observed bond distances are in good agreement with those expected and indicate localisation of double and single bonds, the lengths of the latter being in most cases significantly longer than those of the former. One "single bond", C(4)–C(6), which lies between a carbonyl group and a double bond is rather short compared to the other single bonds thus suggesting conjugation, which is confirmed by the compound's IR and UV spectra.[1] The C–OH bond distances are normal,[3] and although the two C–Br bond distances are not identical the difference between them is hardly significant. Nor are the dimensions of the dioxan molecule significantly different from those reported in the literature.[4]

An absorption band at 206 nm in the UV spectrum of the compound indicates photoexcited transannular π-orbital overlap[5] between the double bond,

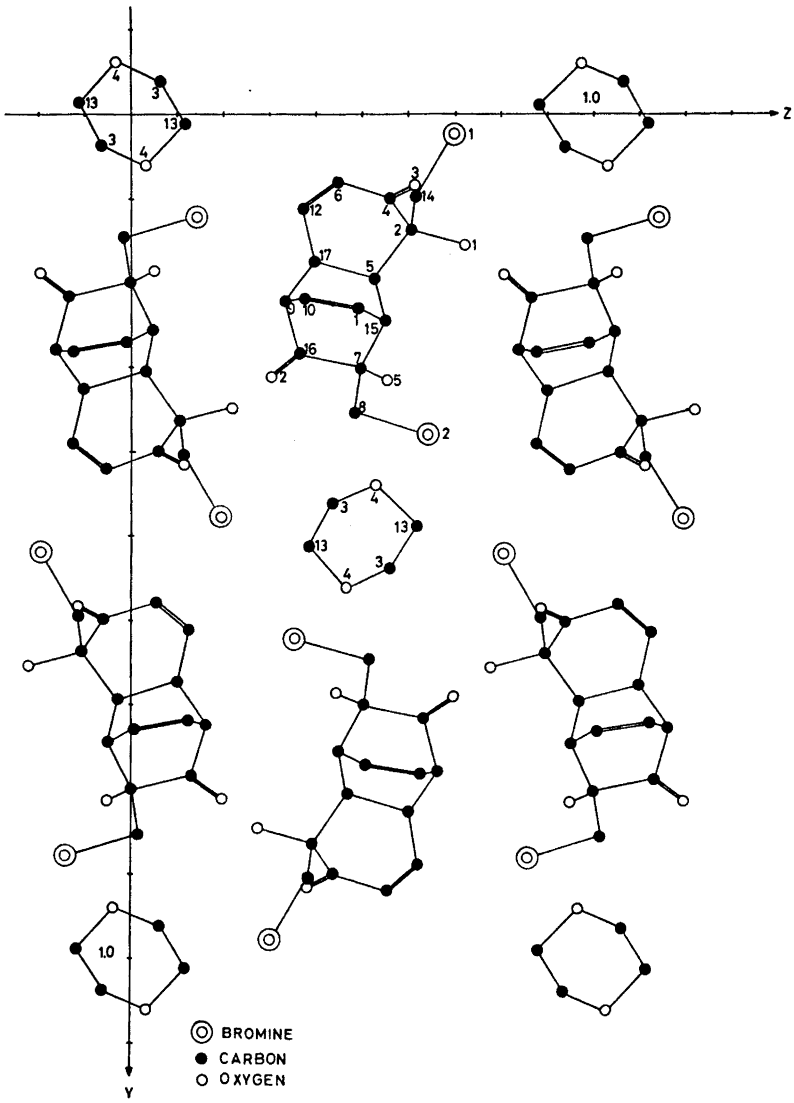

Fig. 2. A projection of a unit cell of "dibromide" along the x-axis.

C(1) – C(10), and the carbonyl group, C(16) – O(2), of the homoconjugated system C(1) – C(10) – C(9) – C(16) – O(2). This is in harmony with the short O(2) – C(10) distance of 3.58 Å. From Fig. 1 it is apparent that the other carbonyl group, C(4) – O(3), also lies near the C(1) – C(10) double bond and, moreover, its direction is such that would make interaction with the C(1) – C(10) double bond feasible. Since the O(3) – C(10) distance is 3.54 Å and thus of the same

order of magnitude as the O(2)–C(10) distance, it seems possible that transannular interaction also occurs between the C(1)–C(10) double bond and the C(4)–O(3) carbonyl group.

Hydrogen bonding occurs between the O(3) carbonyl oxygen and the O(1) hydroxyl oxygen, the O(1)–O(3) distance being 2.65 Å, this hydrogen bond completing a five-ring with O(3), C(4), C(2), and O(1). There is a further hydrogen bond between the O(5) hydroxyl group and O(4) in the dioxan ring (Fig. 2), the O(5)–O(4) distance also being rather short (2.83 Å). Although the O(5)–O(2) distance is only 2.95 Å, the possibility that O(5) is bonded to O(2) can probably be disregarded owing to the unfavourable bond angle.

In the OH-stretching region, the IR spectrum of the compound shows bands at 3470 cm^{-1} and 3340 cm^{-1}. The "dibromide", crystallized from benzene solution, showed IR-bands at 3458 and 3410 cm^{-1}. An acetyl compound of the "dibromide" in which the hydrogen atom bound to the O(1) atom was substituted by an acetyl group showed one band at 3510 cm^{-1}. Thus the band found at 3340 cm^{-1} for the "dibromide" dioxan compound must be ascribable to the stretching frequency of the hydroxyl group containing the oxygen atom O(5) and bonded by a hydrogen bond to the oxygen atom O(4) of the dioxan molecule. The other band at 3470 cm^{-1} is then due to the hydroxyl group involved in the intramolecular hydrogen bond ···O(1)–H···O(3).

From the relationship existing between the O–O interatomic distance and the IR stretching frequency [6] it is apparent that the band at 3340 cm^{-1} corresponds to an O–O interatomic distance of 2.81 Å which is in good agreement with that found between O(4) of the dioxan molecule and the hydroxyl oxygen, O(5). The other hydroxyl band would appear to correspond to an O–O distance of 2.86 Å. There is, however, no more such distance to be found in the structure. This band can, nevertheless, be correlated with the intramolecular hydrogen bond between the hydroxyl group, O(1) and the carbonyl oxygen atom O(3), since a different relationship between frequency and interatomic distance exists for such bonds.[6]

The dioxan molecule lies in a hollow formed by the bromine atoms (Fig. 2) and is bound by comparatively strong hydrogen bonds through hydroxyl groups to two different molecules of the compound. One molecule of dioxan and two of "dibromide" thus form a sort of complex.

Acknowledgements. We wish to express our sincere gratitude to Professor Erich Adler for very valuable discussions. A grant from the *Research Fund of Chalmers University of Technology* is gratefully acknowledged.

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Received December 10, 1969.