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The Crystal Structure of 1,4-Bis(*p*-bromophenoxy)butane

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The structure of 1,4-Bis(*p*-bromophenoxy)butane has been determined by means of a single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group *Cc*, with four molecules per unit cell: $a=13.426$, $b=15.249$, $c=7.650$ Å, and $\beta=89.39°$. The structure has been solved by the heavy-atom method. The final discrepancy index is 0.068 for 970 non-zero reflections. The conformation of the methylene chain in the $-O(CH_2)_4O-$ group is *gauche-trans-gauche*, with internal rotation angles of 61.0, 181.0, and 55.2° respectively.

High polymers consisting of the repeating unit $X-C_6H_4-O-(CH_2)_n-O-C_6H_4-X$ generally show high melting and glass-transition points and high elastic moduli. It is generally accepted that this behavior is not only due to the rigidity of the benzene rings in the molecular chains, but also to the length and conformation of the methylene chain between the phenoxy groups.[1-4]

As a crystallographic approach to this problem, Yasuoka *et al.* have determined the crystal structures of a series of model compounds of the above type of polymer. Among the compounds are 1,2-Bis(phenoxy)-ethane,[5] 1,2-Bis(*p*-chlorophenoxy)ethane,[6] and 1,3-Bis-(*p*-bromophenoxy)propane.[7] As a part of this series of studies, the crystal structure analysis of 1,4-Bis(*p*-bromophenoxy)butane, $BrC_6H_4O(CH_2)_4OC_6H_4Br$ was undertaken by means of X-ray diffraction.

Experimental

Single crystals of 1,4-Bis(*p*-bromophenoxy)butane were recrystallized from a methanol-benzene solution. From oscil-

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[1] T. Ando and S. Kataoka, *Kogyo Kagaku Zasshi*, **65**, 2057 (1962).
[2] T. Ando and S. Kataoka, *ibid.*, **66**, 1724 (1963).
[3] T. Ando and S. Kataoka, *Nippon Kagaku Zasshi*, **87**, 764 (1966).
[4] I. Sakurada, I. Ito, and K. Nakamae, *Makromol. Chem.*, **75**, 1 (1964).
[5] N. Yasuoka, T. Ando, and S. Kuribayashi, This Bulletin **40**, 270 (1967).
[6] N. Yasuoka, T. Ando, and S. Kuribayashi, **40**, *ibid.*, 265 (1967).
[7] Preprints for the 22nd Annual Meeting of the Chemical Society of Japan, Tokyo (April, 1969), and unpublished work.

lation and Weissenberg photographs, the approximate dimensions of the unit cell were determined; they were later redetermined precisely by using a Rigaku on-line controlled four-circle diffractometer. The crystal belongs to the monoclinic system. The systematic absences of reflections, $h+k \neq 2n$ for hkl and $l \neq 2n$ for $h0l$, indicate that the probable space group is $C2/c$ or Cc. The density of the crystal was measured by the flotation method in a carbon tetrachloride-bromoform solution at room temperature. The crystal data are listed in Table 1.

Table 1. Crystal data

$Br_2C_{16}H_{16}O_2$	Mol wt 400.1
	mp 118—120°C
$a=13.426$ Å	$D_m=1.70\text{g}\cdot\text{cm}^{-3}$
$b=15.249$	$D_x=1.69\text{g}\cdot\text{cm}^{-3}$
$c=7.650$	$Z=4$
$\beta=89.39°$	Space group Cc

The three-dimensional intensity data were at first collected by multiple-film equi-inclination Weissenberg photographs. Subsequently, the redetermination of the intensity data was carried out using a Rigaku single-crystal diffractometer. A total of 1034 independent reflections (970 non-zero reflections) were collected by means of zirconium-filtered Mo$K\alpha$ radiation. The dimensions of the crystal used were $0.1 \times 0.12 \times 0.20$ mm. The intensities were corrected for usual Lorentz and polarization factors, but the absorption correction was ignored (the linear absorption coefficient was $\mu=54.6\ \text{cm}^{-1}$ for Mo$K\alpha$).

Structure Determination and Refinement

Though $C2/c$ or Cc was postulated for the structure at the beginning, the space group is determined to be Cc, since the center of symmetry is not found by the N(z) test and since it is impossible to solve the Patterson map if the space group is $C2/c$.

The approximate coordinates of the two bromine atoms were determined from two-dimensional Patterson maps, $P(u,v)$ and $P(u,w)$. The coordinates of the other non-hydrogen atoms were determined by the successive use of Fourier syntheses. Thus, the molecular shape was determined at this stage, and the discrepancy index, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was 0.21. Further refinement was carried out by using the counter data.

The atomic and isotropic thermal parameters were refined by a block-diagonal least-squares procedure. After seven cycles, the R index was reduced to 0.136 for 970 non-zero reflections. At this stage, anisotropic thermal parameters for non-hydrogen atoms were introduced; six subsequent cycles of the refinement gave $R=0.076$. The function minimized was $\Sigma w\Delta^2$, where the weighting scheme used was:

$$w = 200.0/|F_0| \quad (|F_0| \geqq 200.0),$$
$$w = 1 \quad (200.0 > |F_0| > 4.0), \text{ and}$$
$$w = 0.2 \quad (|F_0| \leqq 4.0).$$

The atomic scattering factors for all atoms were taken from the International Tables for X-ray Crystallography.[8]

A difference Fourier synthesis (ρ_o-ρ_c) was computed; however, several hydrogen atoms among the total of sixteen could not be found as sharp peaks. Therefore, the coordinates of the hydrogen atoms were fixed; all the C–H bond lengths were taken as 1.08 Å. The anomalous dispersion of the bromine atoms ($\Delta f'=-0.30$ and $\Delta f''=2.60$) was introduced in the refinement, and the R index reached 0.068. At this stage, it was found that the parameter shifts were insignificant compared to the estimated standard deviations, and so the refinement was terminated.

Table 2. The atomic parameters in fraction of cell edges and their estimated standard deviations (in Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Br(1)	0.0000	0.003	0.0838	0.002	−0.5000	0.003
Br(2)	0.1563	0.003	0.1507	0.002	1.1534	0.003
C (1)	0.8899	0.021	0.1030	0.019	−0.3364	0.017
C (2)	0.9161	0.017	0.1311	0.017	−0.1714	0.021
C (3)	0.8359	0.024	0.1468	0.021	−0.0546	0.017
C (4)	0.7420	0.013	0.1281	0.021	−0.1010	0.019
C (5)	0.7183	0.020	0.0991	0.022	−0.2695	0.020
C (6)	0.7968	0.018	0.0867	0.020	−0.3853	0.019
C (7)	0.2466	0.016	0.1410	0.015	0.9706	0.016
C (8)	0.2284	0.020	0.0947	0.022	0.8310	0.022
C (9)	0.2985	0.020	0.0869	0.018	0.6830	0.018
C (10)	0.3846	0.018	0.1288	0.017	0.6986	0.021
C (11)	0.4093	0.019	0.1778	0.021	0.8454	0.021
C (12)	0.3392	0.020	0.1829	0.019	0.9803	0.021
C (13)	0.6740	0.021	0.1740	0.017	0.1690	0.024
C (14)	0.5765	0.023	0.1755	0.018	0.2775	0.020
C (15)	0.5325	0.019	0.0827	0.020	0.3065	0.021
C (16)	0.4405	0.020	0.0850	0.019	0.4127	0.020
O (1)	0.6578	0.014	0.1388	0.014	0.0024	0.014
O (2)	0.4575	0.013	0.1285	0.015	0.5747	0.012

Table 3. The anisotropic thermal parameters, of the form: $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{23}kl+B_{13}hl\}$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br(1)	0.0088	0.0076	0.0287	−0.0006	0.0115	0.0012
Br(2)	0.0087	0.0060	0.0209	−0.0013	0.0076	−0.0017
C(1)	0.0092	0.0041	0.0110	−0.0021	0.0089	−0.0008
C(2)	0.0044	0.0036	0.0255	−0.0021	−0.0053	−0.0073
C(3)	0.0100	0.0061	0.0102	0.0016	0.0040	−0.0033
C(4)	0.0008	0.0080	0.0213	0.0029	−0.0051	0.0014
C(5)	0.0058	0.0062	0.0204	0.0009	−0.0067	−0.0038
C(6)	0.0046	0.0057	0.0163	0.0023	−0.0033	−0.0008
C(7)	0.0054	0.0014	0.0168	−0.0008	0.0015	0.0036
C(8)	0.0056	0.0065	0.0260	−0.0011	0.0147	−0.0021
C(9)	0.0078	0.0038	0.0144	0.0039	−0.0041	−0.0008
C(10)	0.0049	0.0028	0.0258	0.0029	−0.0020	0.0088
C(11)	0.0052	0.0058	0.0208	0.0000	−0.0071	0.0059
C(12)	0.0068	0.0040	0.0226	−0.0007	−0.0081	0.0007
C(13)	0.0062	0.0033	0.0269	0.0040	−0.0057	−0.0009
C(14)	0.0095	0.0029	0.0188	0.0014	0.0096	0.0034
C(15)	0.0055	0.0047	0.0242	0.0023	0.0087	0.0076
C(16)	0.0064	0.0047	0.0200	−0.0035	0.0025	−0.0018
O(1)	0.0063	0.0063	0.0195	0.0027	−0.0009	0.0035
O(2)	0.0058	0.0075	0.0159	−0.0008	0.0027	0.0101

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8) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham (1961), p. 202.

Table 4. The observed and calculated structure factors

K	FO	FC
H,L=	0	0
2	12	12
4	355	363
6	0	10
8	0	5
10	15	19
12	51	49
14	28	26
16	3	15
H,L=	1	0
1	84	80
3	64	64
5	93	90
7	46	45
9	31	32
11	16	15
13	37	40
15	12	4
H,L=	2	0
0	39	39
2	78	79
4	41	41
6	125	125
8	43	42
10	63	65
12	20	24
14	14	14
16	12	15
H,L=	3	0
1	28	30
3	64	65
5	45	46
7	104	103
9	26	24
11	48	47
13	15	13
15	0	2
H,L=	4	0
0	123	124
2	105	106
4	97	94
6	155	153
8	54	52
10	63	62
12	18	22
14	15	11
H,L=	5	0
1	78	82
3	53	54
5	37	43
7	43	46
9	34	34
11	21	23
13	25	25
15	0	0
H,L=	6	0
0	123	126
2	1	4
4	59	61
6	7	13
8	24	24
10	27	25
12	32	34
14	13	18
H,L=	7	0
1	90	90
3	51	49
5	40	43
7	18	19
9	18	17
11	0	15
H,L=	8	0
0	77	77
2	27	26
4	48	51
6	47	46
8	9	9
10	22	23
12	0	8
H,L=	9	0
1	30	35
3	40	38
5	34	36
7	58	58
9	11	12
11	27	31
H,L=	10	0
0	9	9
2	35	33
4	17	18
6	56	59
8	19	22
10	26	32
H,L=	11	0
1	36	33
3	14	13
5	30	31
7	10	13
9	6	12
H,L=	12	0
0	50	52
2	12	8
4	30	31
6	9	17
8	13	10
H,L=	13	0
1	32	25
3	0	13
5	20	19
7	7	4
H,L=	14	0
0	33	28
2	8	6
4	19	20
H,L=	0	1
2	10	12
4	243	236
6	45	43
8	152	148
10	49	46
12	38	38
14	27	22
16	0	2
H,L=	1	1
1	79	80
3	98	100
5	69	69
7	42	42
9	44	45
11	34	31
13	19	13
15	15	21
H,L=	2	1
2	347	385
4	94	84
6	105	104
8	44	41
10	28	28
12	25	29
14	25	24
16	21	17
H,L=	3	1
1	92	95
3	132	131
5	64	64
7	38	37
9	34	33
11	39	42
13	0	12
15	35	38
H,L=	4	1
2	141	143
4	72	68
6	37	34
8	67	64
10	28	27
12	26	28
14	13	19
H,L=	5	1
1	31	30
3	48	50
5	85	84
7	38	39
9	55	55
11	16	14
13	4	5
15	0	6
H,L=	6	1
2	92	93
4	92	95
6	48	46
8	66	68
10	26	25
12	0	11
14	4	7
H,L=	7	1
1	46	48
3	46	48
5	34	36
7	20	22
9	31	31
11	25	21
13	1	9
H,L=	8	1
2	65	61
4	15	17
6	16	16
8	17	20
10	20	23
12	20	16
H,L=	9	1
1	50	48
3	45	42
5	15	18
7	0	1
9	9	8
11	21	20
H,L=	10	1
2	52	48
4	29	28
6	14	12
8	6	16
10	11	10
H,L=	11	1
1	15	14
3	19	15
5	34	34
7	11	10
9	30	31
H,L=	12	1
2	15	12
4	37	33
6	18	15
8	30	28
H,L=	13	1
1	9	11
3	13	11
5	11	8
7	15	10
H,L=	14	1
2	21	16
H,L=	0	2
0	103	101
2	51	50
4	71	68
6	69	69
8	21	23
10	33	32
12	14	14
14	14	17
H,L=	1	2
1	49	49
3	92	91
5	62	60
7	152	148
9	22	23
11	77	77
13	15	7
15	12	12
H,L=	2	2
0	104	104
2	112	110
4	19	20
6	167	159
8	48	46
10	70	65
12	36	40
14	0	7
H,L=	3	2
1	72	75
3	75	75
5	32	35
7	85	88
9	27	23
11	42	47
13	19	21
15	4	8
H,L=	4	2
0	139	146
2	11	6
4	97	99
6	24	23
8	21	22
10	31	33
12	18	14
14	14	18
H,L=	5	2
1	102	106
3	61	62
5	65	68
7	55	53
9	9	13
11	33	33
13	37	40
H,L=	6	2
0	123	121
2	37	35
4	69	64
6	62	61
8	15	12
10	36	35
12	21	17
14	0	12
H,L=	7	2
1	16	18
3	55	55
5	32	33
7	50	48
9	17	19
11	12	11
13	12	6
H,L=	8	2
0	36	38
2	26	26
4	26	27
6	40	42
8	20	20
10	10	17
12	6	7
H,L=	9	2
1	30	29
3	26	23
5	21	22
7	26	27
9	11	11
11	0	12
H,L=	10	2
0	40	42
2	17	10
4	21	22
6	15	15
8	0	11
10	12	10
H,L=	11	2
1	33	31
3	17	24
5	2	12
7	6	7
9	4	7
H,L=	12	2
0	28	28
2	3	12
4	13	17
6	21	18
8	5	7
H,L=	13	2
1	7	8
3	20	17
5	10	5
H,L=	14	2
0	8	10
H,L=	0	3
2	112	109
4	18	17
6	13	15
8	22	22
10	27	27
12	19	21
14	17	19
H,L=	1	3
1	121	121
3	139	133
5	36	34
7	29	25
9	13	15
11	37	39
13	0	2
15	23	28
H,L=	2	3
2	108	111
4	60	59
6	35	31
8	41	41
10	19	15
12	14	9
14	5	14
H,L=	3	3
1	35	38
3	38	37
5	96	95
7	39	40
9	68	69
11	15	16
13	22	20
H,L=	4	3
2	48	48
4	69	69
6	11	11
8	53	53
10	27	29
12	10	12
14	14	16
H,L=	5	3
1	49	47
3	55	54
5	72	71
7	4	14
9	74	75
11	12	17
13	29	31
H,L=	6	3
2	70	70
4	28	29
6	24	29
8	25	25
10	12	15
12	3	16
H,L=	7	3
1	52	52
3	36	37
5	38	37
7	0	6
9	31	34
11	26	26
13	18	18
H,L=	8	3
2	41	43
4	34	37
6	6	6
8	29	29
10	8	9
12	0	8
H,L=	9	3
1	21	22
3	24	25
5	31	29
7	22	21
9	5	16
11	11	9
H,L=	10	3
2	13	7
4	17	19
6	21	11
8	17	17
10	9	9
H,L=	11	3
1	11	7
3	0	9
5	10	16
7	14	9
H,L=	12	3
2	24	26
4	0	6
6	0	5
H,L=	13	3
1	15	17
3	17	13
H,L=	0	4
0	65	63
2	39	37
4	43	44
6	67	64
8	25	25
10	37	35
12	8	11
14	0	9
H,L=	1	4
1	59	62
3	66	67
5	36	36
7	56	56
9	21	23
11	18	17
13	24	25
H,L=	2	4
0	98	102
2	0	2
4	57	56
6	15	10
8	8	11
10	13	15
12	23	22
14	12	8
H,L=	3	4
1	96	97
3	54	53
5	54	53
7	19	17
9	3	8
11	0	11
13	17	19
H,L=	4	4
0	86	84
2	26	29
4	51	49
6	47	48
8	5	1
10	18	20
12	0	11
H,L=	5	4
1	25	24
3	44	45
5	23	22
7	45	43
9	11	12
11	18	17
13	21	12
H,L=	6	4
0	20	23
2	28	27
4	4	8
6	46	46
8	9	7
10	23	23
12	0	7
H,L=	7	4
1	37	39
3	39	38
5	30	37
7	49	49
9	15	7
11	31	30
H,L=	8	4
0	51	51
2	0	13
4	31	32
6	24	19
8	16	7
10	9	10
H,L=	9	4
1	22	20
3	29	27
5	12	9
7	15	14
9	18	17
H,L=	10	4
0	21	20
2	13	12
4	19	11
6	19	17
8	0	2
H,L=	11	4
1	13	10
3	0	8
5	12	10
7	13	14
H,L=	12	4
0	3	3
2	12	5
4	0	7
H,L=	0	5
2	54	53
4	58	57
6	29	25
8	53	53
10	17	14
12	24	25
H,L=	1	5
1	15	15
3	25	27
5	59	54
7	20	25
9	44	42
11	19	14
13	14	11
H,L=	2	5
2	34	33
4	50	49
6	28	29
8	41	42
10	19	16
12	18	15
H,L=	3	5
1	27	33
3	30	32
5	40	40
7	14	15
9	22	23
11	18	23
H,L=	4	5
2	55	58
4	15	13
6	14	11
8	12	10
10	15	18
12	4	5
H,L=	5	5
1	29	32
3	22	24
5	0	14
7	9	5
9	0	4
11	12	7
H,L=	6	5
2	53	58
4	21	26
6	17	20
8	21	19
10	0	4
H,L=	7	5
1	16	19
3	25	28
5	18	20
7	16	15
9	15	19
H,L=	8	5
2	22	21
4	19	21
6	13	6
8	21	21
H,L=	9	5
1	25	25
3	15	21
5	19	23
7	13	11
H,L=	10	5
2	27	26
4	6	11
6	0	7
H,L=	11	5
1	13	17
3	14	10
H,L=	0	6
0	84	81
2	11	8
4	47	45
6	17	15
8	0	5
10	11	13
H,L=	1	6
1	45	44
3	34	32
5	22	26
7	4	8
9	7	11
11	16	6
H,L=	2	6
0	42	42
2	12	16
4	30	28
6	28	31
8	8	9
10	25	27
H,L=	3	6
1	3	7
3	24	24
5	17	16
7	31	31
9	20	14
H,L=	4	6
0	11	11
2	21	19
4	12	15
6	36	34
8	16	16
10	18	18
H,L=	5	6
1	0	17
3	19	18
5	10	8
7	16	11
9	5	10
H,L=	6	6
0	32	33
2	0	5
4	18	17
6	13	10
8	11	9
H,L=	7	6
1	12	6
3	7	5
5	0	3
7	14	8
H,L=	8	6
0	39	37
2	17	10
4	27	26
6	22	15
H,L=	9	6
1	18	11
3	0	6
5	0	8
H,L=	10	6
0	0	3
H,L=	0	7
2	21	21
4	28	30
6	16	15
8	21	25
H,L=	1	7
1	26	26
3	23	15
5	25	22
7	16	9
H,L=	2	7
2	40	41
4	0	6
6	10	13
8	16	9
H,L=	3	7
1	25	24
3	23	25
5	15	10
7	9	10
H,L=	4	7
2	19	24
4	9	10
6	17	11
H,L=	5	7
1	4	11
3	11	3
5	13	18
H,L=	6	7
2	0	5
4	12	14
H,L=	7	7
1	0	7
3	4	0
H,L=	0	8
0	15	16
2	7	5
4	15	11
H,L=	1	8
1	10	5
3	13	11
H,L=	2	8
0	11	16
2	17	13
H,L=	3	8
1	13	9
H,L=	-1	1
1	31	31
3	33	33
5	147	142
7	18	19
9	120	115
11	14	12
13	32	32
15	0	11
H,L=	-2	1
2	69	71
4	148	141
6	65	61
8	105	101
10	28	25
12	33	33
14	0	6
16	14	11
H,L=	-3	1
1	96	94
3	84	82
5	54	53
7	31	29
9	31	36
11	40	40
13	8	8
15	17	19
H,L=	-4	1
2	157	153
4	18	18
6	20	21
8	7	12
10	52	49
12	28	25
14	32	33

Table 4. (Continued)

K	FO	FC
H,L= -5		1
1	121	119
3	107	107
5	38	37
7	13	12
9	21	19
11	32	35
13	0	6
15	21	22
H,L= -6		1
2	78	82
4	91	90
6	50	48
8	68	66
10	15	14
12	21	18
14	9	5
H,L= -7		1
1	48	48
3	68	69
5	89	86
7	46	43
9	67	65
11	17	15
13	16	15
H,L= -8		1
2	47	47
4	56	55
6	36	33
8	55	52
10	11	16
12	18	22
H,L= -9		1
1	32	32
3	60	59
5	36	36
7	32	31
9	27	27
11	18	17
H,L=-10		1
2	92	93
4	0	5
6	25	24
8	0	9
10	16	16
H,L=-11		1
1	46	47
3	50	50
5	14	14
7	18	15
9	0	2
H,L=-12		1
2	29	30
4	19	17
6	4	19
8	17	13
H,L=-13		1
1	13	10
3	19	14
5	16	15
H,L=-14		1
2	0	4
H,L= -1		2
1	131	132
3	77	75
5	64	60
7	25	27
9	40	37
11	2	7
13	43	42
15	6	6
H,L= -2		2
0	185	187
2	19	19
4	106	101
6	20	21
8	21	18
10	16	19
12	39	41
14	15	17
H,L= -3		2
1	133	136
3	94	94
5	64	63
7	45	45
9	24	23
11	8	9
13	32	32
15	9	7
H,L= -4		2
0	107	112
2	77	75
4	73	72
6	104	104
8	34	31
10	46	42
12	17	15
14	12	12
H,L= -5		2
1	78	76
3	91	89
5	82	77
7	103	101
9	33	34
11	39	42
13	12	12
H,L= -6		2
0	138	135
2	30	32
4	75	74
6	69	68
8	26	26
10	45	43
12	19	15
14	16	14
H,L= -7		2
1	69	71
3	51	51
5	57	57
7	52	54
9	15	16
11	23	25
13	25	26
H,L= -8		2
0	117	116
2	12	10
4	63	63
6	13	13
8	0	11
10	4	13
12	22	25
H,L= -9		2
1	81	81
3	50	50
5	43	42
7	0	6
9	12	9
11	0	2
H,L=-10		2
0	25	19
2	34	34
4	12	20
6	57	56
8	24	20
10	23	24
H,L=-11		2
1	7	15
3	22	22
5	18	17
7	41	37
9	11	4
H,L=-12		2
0	7	15
2	16	16
4	10	10
6	26	28
8	11	10
H,L=-13		2
1	11	16
3	16	18
5	14	16
H,L=-14		2
0	26	27
H,L= -1		3
1	104	105
3	102	99
5	77	77
7	29	26
9	36	36
11	27	30
13	2	1
15	21	19
H,L= -2		3
2	84	82
4	81	82
6	35	34
8	69	69
10	24	23
12	22	21
14	17	12
H,L= -3		3
1	61	59
3	46	46
5	105	103
7	45	46
9	70	69
11	16	16
13	17	16
H,L= -4		3
2	135	131
4	98	94
6	34	32
8	82	79
10	24	31
12	29	30
14	14	13
H,L= -5		3
1	85	89
3	92	94
5	63	66
7	29	30
9	46	45
11	28	30
13	0	12
H,L= -6		3
2	86	88
4	17	14
6	11	13
8	9	6
10	31	30
12	12	18
H,L= -7		3
1	73	73
3	60	60
5	42	43
7	3	8
9	26	25
11	26	20
13	4	12
H,L= -8		3
2	38	39
4	79	80
6	19	18
8	63	62
10	24	27
12	15	13
H,L= -9		3
1	10	11
3	32	32
5	48	47
7	22	21
9	35	38
11	12	9
H,L=-10		3
2	2	3
4	30	31
6	18	16
8	29	25
10	20	19
H,L=-11		3
1	22	26
3	26	23
5	26	25
7	0	10
H,L=-12		3
2	43	43
4	5	15
6	11	10
H,L=-13		3
1	28	26
3	29	24
H,L= -1		4
1	13	14
3	69	66
5	44	42
7	85	81
9	24	24
11	34	34
13	8	9
H,L= -2		4
0	84	90
2	61	59
4	55	52
6	95	93
8	26	26
10	43	49
12	18	21
14	15	14
H,L= -3		4
1	89	92
3	73	73
5	50	52
7	47	44
9	26	27
11	23	19
13	27	26
H,L= -4		4
0	111	115
2	24	22
4	60	60
6	23	21
8	17	17
10	12	13
12	29	31
H,L= -5		4
1	60	62
3	55	56
5	37	36
7	62	62
9	8	13
11	40	40
13	16	19
H,L= -6		4
0	74	76
2	44	44
4	45	42
6	71	72
8	25	26
10	36	32
12	24	22
H,L= -7		4
1	5	10
3	33	33
5	33	27
7	39	40
9	0	14
11	18	15
H,L= -8		4
0	31	31
2	28	32
4	1	12
6	51	53
8	31	24
10	22	20
H,L= -9		4
1	47	47
3	34	34
5	24	24
7	25	24
9	17	8
H,L=-10		4
0	54	60
2	17	12
4	35	35
6	21	20
8	0	3
H,L=-11		4
1	30	33
3	24	23
5	11	14
7	0	5
H,L=-12		4
0	33	36
2	15	12
4	25	23
H,L= -1		5
1	66	65
3	51	52
5	37	35
7	24	21
9	11	8
11	16	21
13	5	3
H,L= -2		5
2	98	96
4	20	20
6	21	19
8	13	11
10	26	25
12	14	15
H,L= -3		5
1	56	58
3	69	68
5	59	57
7	33	30
9	46	50
11	14	16
H,L= -4		5
2	49	50
4	52	53
6	24	26
8	44	44
10	16	18
12	13	13
H,L= -5		5
1	17	18
3	28	29
5	32	30
7	19	20
9	21	17
11	0	6
H,L= -6		5
2	31	33
4	64	64
6	16	16
8	53	50
10	14	18
H,L= -7		5
1	46	48
3	42	45
5	22	26
7	10	8
9	26	22
H,L= -8		5
2	56	58
4	6	14
6	14	13
8	4	12
H,L= -9		5
1	27	28
3	22	23
5	16	19
7	2	6
H,L=-10		5
2	36	39
4	27	26
6	23	18
H,L=-11		5
1	0	7
3	16	18
H,L= -1		6
1	49	50
3	44	43
5	33	33
7	29	32
9	9	9
11	23	16
H,L= -2		6
0	26	24
2	24	25
4	24	23
6	44	44
8	14	15
10	19	23
H,L= -3		6
1	43	44
3	18	17
5	44	44
7	27	29
9	10	13
H,L= -4		6
0	43	44
2	32	31
4	31	30
6	53	51
8	11	12
10	28	24
H,L= -5		6
1	31	35
3	22	25
5	17	14
7	20	18
9	16	13
H,L= -6		6
0	61	65
2	14	3
4	39	37
6	9	5
8	15	7
H,L= -7		6
1	34	31
3	24	22
5	22	21
7	21	20
H,L= -8		6
0	42	42
2	23	17
4	28	30
6	29	30
H,L= -9		6
1	12	7
3	23	22
H,L= -1		7
1	21	18
3	32	33
5	25	22
7	21	19
H,L= -2		7
2	35	32
4	26	27
6	17	15
8	23	23
H,L= -3		7
1	20	23
3	21	19
5	7	10
7	0	3
H,L= -4		7
2	45	44
4	11	10
6	16	15
H,L= -5		7
1	28	28
3	28	31
5	13	18
H,L= -6		7
2	26	28
4	25	23
H,L= -7		7
1	14	10
3	0	13
H,L= -1		8
1	26	21
3	14	11
H,L= -2		8
0	28	32
2	1	6
H,L= -3		8
1	19	20

The final atomic coordinates, along with their estimated standard deviations, are listed in Table 2. The thermal parameters are listed in Table 3. The observed and calculated structure factors are given in Table 4.

The computations of the Patterson function were performed on a NEAC 2200—500 computer at Osaka University, while the Fourier syntheses, least-squares refinements, and other calculations were carried out on a FACOM 230—60 computer at Kyoto University with programs written by Dr. T. Ashida.

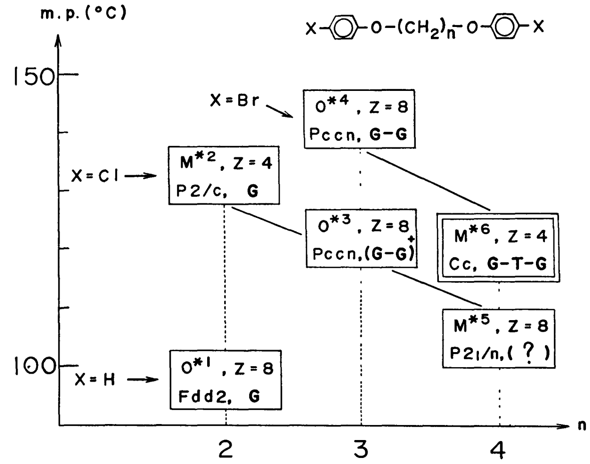

Fig. 1. Crystal data of a series of compounds, X-⌬-O-$(CH_2)_n$-O-⌬-X, correlated with the number of methylene groups, n as well as melting points.

- *1 n: 2, X: H, Orthorhombic, Dm=1.22 g·cm^{-3}, mp: 97.3°C a=34.74, b=12.04, c=5.58 Å[8]
- *2 n: 2, X: Cl, Monoclinic, Dm=1.45 g·cm^{-3}, mp: 132.5°C a=12.79, b=9.89, c=10.37 Å, β=98.2°[9]
- *3 n: 3, X: Cl, Orthorhombic, Dm=1.36 g·cm^{-3}, mp: 121.5°C a=16.83, b=17.64, c=9.60 Å
- *4 n: 3, X: Br, Orthorhombic, Dm=1.75 g·cm^{-3}, mp: 142.5°C a=17.13, b=17.76, c=9.61 Å[10]
- *5 n: 4, X: Cl, Monoclinic, Dm=1.32 g·cm^{-3}, mp: 105.8°C a=12.19, b=20.01, c=12.84 Å, β=92.9°
- *6 n: 4, X: Br, Monoclinic, Dm=1.70 g·cm^{-3}, mp: 118—120°C a=13.43, b=15.25, c=7.65 Å, β=89.4°

$^+$ Supposed conformation on the bases of the fact that Br- and Cl-derivatives are isostructural in the case of n=3.

Discussion

Figure 1 shows the crystal and physical data of a series of homologous compounds, X-C_6H_4-O-$(CH_2)_n$-O-C_6H_4-X (X=H or halogen atom). The crystal structures of the homologues with n=2 had previously been determined.[5,6] For n=3, only the crystal structure of the Br-derivative[7] has been determined; however, the Cl-derivative can be expected to have a similar structure, since they have the same space group, similar unit-cell parameters, and an equal number of chemical units per unit cell, Z, suggesting that these crystals are isostructural.

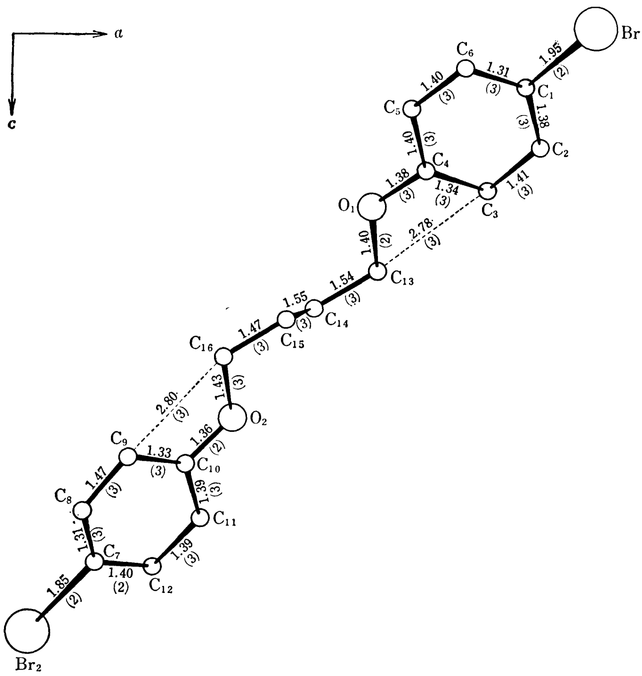

Fig. 2. The molecular shape viewed along the b axis, and bond lengths (Å) with estimated standard deviations (×10^{-2}Å) in the molecule.

In the case of n=4, there is a difference between the crystal data of the Cl- and Br-derivatives. Thus, the space group and the value of Z are $P2_1/n$ and eight respectively, for the Cl-derivative, while they are Cc and four for the Br-derivative. Therefore, it must be noticed that the information on the packing of molecules in the unit cell and the molecular conformation of the Br-derivative obtained in the present study is not always applicable to that of the Cl-derivative.

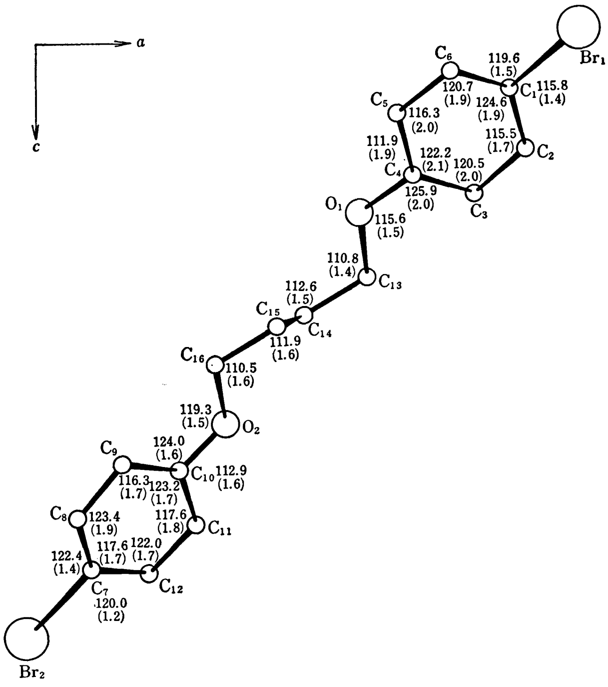

Fig. 3. The molecular shape viewed along the b axis, and bond angles with estimated standard devistions (°) in the molecule.

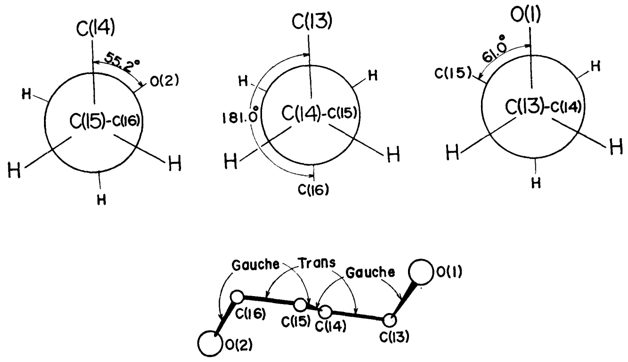

Fig. 4. The conformation of the methylene groups and the internal rotation angles (°).

The molecular shape viewed along the *b* axis is shown in Fig. 2. In Fig. 2 the bond lengths are also given, along with their estimated standard deviations. The bond angles are listed in Fig. 3.

The most remarkable feature of the molecular structure is that the conformation of the methylene groups is in the *gauche-trans-gauche* form (Fig. 4). The internal rotation angles are also shown in Fig. 4. On the other hand, the conformations of the methylene groups found in other, shorter homologues are *gauche* for $n=2$ in $XC_6H_4O(CH_2)_nOC_6H_4X$ and *gauche-gauche* for $n=3$.

The benzene rings are approximately planar, and the best least-squares planes are:

$$0.09254X + 0.94475Y + 0.31445Z + 2.42683 = 0 \quad \text{(benzene 1)}$$

and:

$$0.40188X + 0.81185Y + 0.42354Z + 2.62451 = 0 \quad \text{(benzene 2)}$$

where $X=ax+cx\cos\beta$, $Y=by$, and $Z=cz\sin\beta$. The maximum deviation of the atom from the plane is 0.024 Å for C(3). As is shown in Fig. 2, the non-bonded intramolecular distance from C(3) to C(13) is 2.78 Å, and that one from C(9) to C(16) is 2.80 Å. C(13) and C(16) lie almost on the plane containing the benzene ring, the displacements from the plane being 0.08 and 0.10 Å respectively.

The crystal structure, as viewed along the *b* and *c* axes, is shown in Fig. 5 and 6 respectively. In these figures short intermolecular atomic contacts of less than 4.0 Å are given. As may be seen in Fig. 5, molecules are piled up along the *b* axis; the benzene ring, 1, of a molecule is above the benzene ring, 2, of the other molecule, and the dihedral angle between two benzene rings in a molecule is 20.39°.

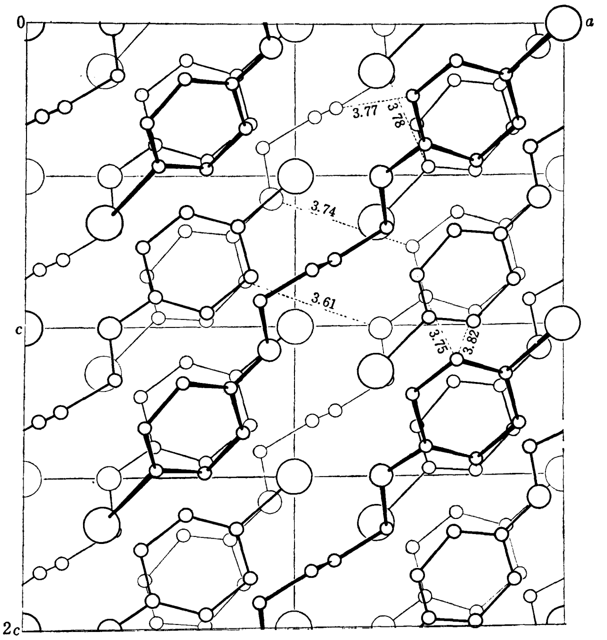

Fig. 5. The crystal structure in the unit cell projected onto the *ac* plane, with some short intermolecular distances (Å).

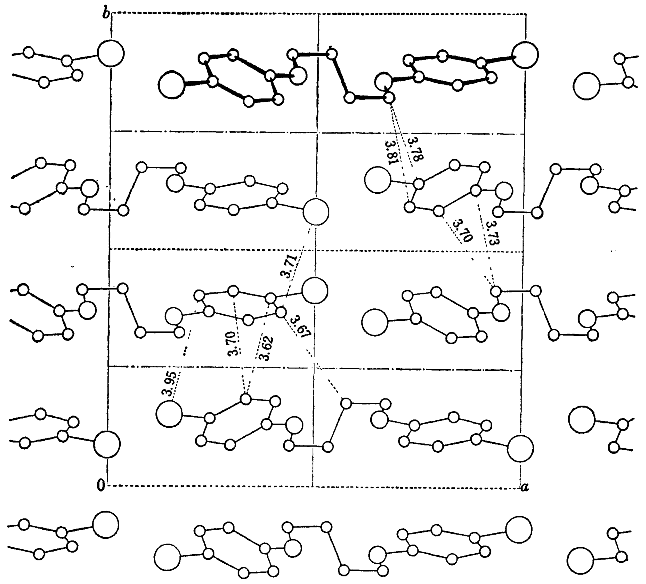

Fig. 6. The crystal structure in the unit cell projected onto the *ab* plane, with some short intermolecular distances(Å).

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