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The Crystal and Molecular Structure of 2,7-Dichlorodibenzo-*p*-dioxin

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The crystal and molecular structure of 2,7-dichlorodibenzo-*p*-dioxin has been determined from three-dimensional single-crystal X-ray diffraction data. This compound crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters $a=3{\cdot}878\pm0{\cdot}003$, $b=6{\cdot}755\pm0{\cdot}009$, $c=10{\cdot}265\pm0{\cdot}015$ Å, $\alpha=99{\cdot}46\pm0{\cdot}01$, $\beta=100{\cdot}63\pm0{\cdot}03$, and $\gamma=99{\cdot}73\pm0{\cdot}03°$, giving a calculated density $\varrho=1{\cdot}647$ g.cm^{-3} for $C_{12}H_6O_2Cl_2$ and $Z=1$. The intensities of 1152 unique reflections were measured, using the θ–2θ scan mode of a Picker automatic diffractometer (Mo $K\alpha$ radiation). The structure was solved from the Patterson function and was refined by full-matrix least-squares analysis to a final R value of 5·7% for the 1030 reflections above background. In the final model, Cl, O, and C atoms were assigned anisotropic thermal parameters, while the hydrogen atoms were restricted to isotropic thermal parameters. The molecules are situated on crystallographic inversion centers; because they are planar, the approximate molecular symmetry is C_{2h}. The C–Cl bond distance is $1{\cdot}742\pm0{\cdot}004$ Å, the C–O distances are 1·380 and 1·382 Å ($\pm0{\cdot}004$), and the six C–C distances vary between 1·370 and 1·397 Å ($\pm0{\cdot}005$). The C–O–C angle in the heterocyclic ring is $116{\cdot}3\pm0{\cdot}2°$.

Introduction

As part of an effort to establish the chemical and biological properties of the chlorinated derivatives of dibenzo-*p*-dioxin, we are undertaking the structure determinations of key compounds in this series by X-ray diffraction. This paper describes the crystal and molecular structure of 2,7-dichlorodibenzo-*p*-dioxin. The preparation, isolation, and X-ray powder diffraction pattern of this compound are being communicated separately (Boer, van Remoortere & Muelder, 1972).

Although the primary purpose of this work is to assist researchers in making a rapid and positive identification of these materials, the molecular conformations are of some interest, since in principle the molecules are capable of folding along their transverse bisectors. Indeed, severe folding is encountered in heterocyclic analogs containing sulfur, such as thianthrenes (Lynton & Cox, 1956; Rowe & Post, 1958) and thioxanthenes (Ternay, Chasar & Sax, 1967), and some slight folding is reported for 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (Cantrell, Webb & Mabis, 1969). On the other hand, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCBD) is planar (Boer, van Remoortere, North & Neuman, 1972).

Experimental

A sample of dichlorodibenzo-*p*-dioxin was received from W. W. Muelder. This material was isolated from sodium 2,4-dichlorophenate that had been heated to 180°C for 16 hours. The dichlorodibenzo-*p*-dioxin forms colorless crystals of a lath-like habit, which tend to be very thin between the {010} faces and are elongated along the *a* axis, corresponding to the shortest dimension of the unit cell. A crystal suitable for X-ray analysis was selected, sealed within a thin-walled Lindemann glass capillary, and aligned on its *a* axis on a Weissenberg goniometer. A preliminary survey of the reciprocal lattice, as recorded on the oscillation and $0kl$ and $1kl$ Weissenberg levels, indicated that the crystal system was triclinic. The crystal was then carefully centered on a Picker automatic four-circle diffractometer, and lattice constants were determined by least-squares refinement of the setting angles of 24 reflections (Mo $K\alpha$ radiation, λ 0·71069 Å).

Crystal data

Molecular formula	$C_{12}H_6O_2Cl_2$
Molecular weight	253·086
Crystal habit	Lath
Crystal size	$1{\cdot}50 \times 0{\cdot}022 \times 0{\cdot}096$ mm (**a**, **b**, and **c** directions)
Space group	$P\bar{1}$ (No. 2-C_i)
Cell constants (reduced cell),	25°C
a	$3{\cdot}878 \pm 0{\cdot}003$ Å
b	$6{\cdot}755 \pm 0{\cdot}009$
c	$10{\cdot}265 \pm 0{\cdot}015$
α	$99{\cdot}46 \pm 0{\cdot}01°$
β	$100{\cdot}63 \pm 0{\cdot}03$
γ	$99{\cdot}73 \pm 0{\cdot}03$
Volume V	$255{\cdot}2 \pm 0{\cdot}1$ Å^3
Density ϱ^{calc}	$1{\cdot}647$ g.cm^{-3} ($Z=1$)
Absorption coefficient μ(Mo $K\alpha$)	$5{\cdot}26$ cm^{-1}
Number of independent reflections observed	1152

The errors given for the cell constants are those determined by the precision of least-squares fit, multiplied by a factor of 10. This factor, chosen arbitrarily, allows for some systematic errors in measurement at a level consistent with our ability to reproduce results with different crystals and/or orientations. The requirement of one formula unit per unit cell can be accommodated by either a molecule situated on an inversion center in space group $P\bar{1}$, or by a molecule in general space in $P1$.

Intensity data were gathered, using the θ–2θ scan mode of the diffractometer and Mo $K\alpha$ radiation selected by the 002 reflection of a highly oriented graphite crystal monochromator. The take-off angle of the X-ray tube was 3°, and a counter aperture $6{\cdot}0 \times 6{\cdot}0$ mm was placed 30 cm from the crystal; 1·5 mm diameter incident- and exit-beam collimators restricted stray radiation. The scan speed was 2° min^{-1} over 2θ angles of $2° + \Delta$, where Δ is the separation of the $K\alpha$ doublet; this range was sufficient to allow for the observed mosaic spread of the crystal. Two stationary-crystal stationary-counter background counts of 10 sec were taken at each end of the scan. The reciprocal lattice was recorded out to $\sin\theta = 0{\cdot}461$, equivalent to the Cu $K\alpha$ sphere. Attenuators were used to prevent counting rates in excess of 12,000 per sec. The test reflection $1\bar{1}\bar{1}$, monitored after every 50 measurements, showed a root-mean-square deviation of intensity of 1%, and a maximum deviation of 3% from the mean. An error $\sigma(I) = [(0{\cdot}02I)_6 + N_o + k^2N_b]^{1/2}$ was assigned to the net intensity $I = N_o - kN_b$ of each reflection, in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where the quantity $\sum w(|F_o| - |F_c|)^2$ was minimized. Here, N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and the F^2 are the intensities corrected for Lorentz and polarization effects by the expression $(\mathrm{Lp})^{-1} = \sin 2\theta(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta \cos^2 2\theta_m)$, where $2\theta_m$ is the monochromator setting angle. The 122 reflections for which $I < 0$ or $I/\sigma(I) < 2{\cdot}0$ were denoted absent and omitted from the refinement. An absorption correction was applied to the data. Transmission factors ranged from 0·942 to 0·986. No correction for secondary extinction appeared necessary, and none was applied. An overall scale factor and temperature factor were computed by Wilson's (1942) method. The intensity statistics matched an ideal centric distribution much more closely than an acentric distribution.

Quantity	Found	Theoretical (centric)	Theoretical (acentric)
$\langle\lvert E\rvert\rangle$	0·828	0·798	0·886
$\langle E^2\rangle$	1·000	1·000	1·000
$\langle\lvert E^2-1\rvert\rangle$	0·911	0·968	0·736
% > 1	29·69	32·00	37·00
% > 2	4·95	5·00	1·80
% > 3	0·09	0·30	0·01

Stringent precautions are recommended to avoid exposure of laboratory personnel to chlorinated dioxins. The procedures followed during this experiment were identical to those described for the X-ray diffraction study of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Boer *et al.*, 1972).

Solution and refinement of the structure

The C, O, and Cl atoms were located from their vector interactions with Cl in a three-dimensional normal-sharpened Patterson function. A trial structure was generated by using these vectors to position an idealized model of the molecule (with normal bond distances and angles, and including hydrogen atoms). Because the Patterson synthesis was consistent with the presence of an inversion center, refinement was begun assuming space group $P\bar{1}$. The initial values of R for this model were $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}239$ and $R_2 = \{\sum w[F_o - F_c]^2/\sum wF_o^2\}^{1/2} = 0{\cdot}259$. In successive cycles of full-matrix least-squares refinement, we introduced the heavy-atom positions, the heavy-atom isotropic temperature factors, the hydrogen positions, and finally the hydrogen isotropic temperature factors as variables. Four additional cycles of isotropic refinement with these 45 variables converged at $R_1=0{\cdot}1284$ and $R_2=0{\cdot}1309$, and gave reasonable numbers (see below) for interatomic distances and angles and for the thermal parameters.

At this time we undertook further tests to determine whether the true space group might be $P1$. Refinement of the 86 variables in the acentric model converged to $R_1=0{\cdot}1153$ for the 1030 reflections above background. The ratio $R=R_1(\text{centric})/R_2(\text{acentric})=1{\cdot}1136$ is well in excess of $\mathscr{R}_{41,944,0.01}=1{\cdot}0336$ extrapolated from Hamilton's (1965) tables (41 is the dimension of the hypothesis and 944 is the number of degrees of freedom), and it implies that we can reject the hypothesis that the space group is centric with less than a 1% probability of error. Nevertheless, inspection of the results after refinement in $P\bar{1}$ showed clearly that the acentric model was inappropriate for determining meaningful metric or thermal parameters for dichlorodibenzo-*p*-dioxin. This point is brought out in Table 1, where high and low values of selected parameters from the $P1$ and $P\bar{1}$ refinements are summarized, and where certain numbers from the acentric refinement, which ought to be equivalent or nearly so, can be seen to exhibit an unreasonably large range of values. The explanation for this scatter is believed to be the high correlations that occur between atomic parameters related by the molecular center. In addition, the system may be attempting to compensate for anisotropic thermal motion. In view of these results, we decided to continue refinement in space group $P\bar{1}$. Because reasonable values were obtained for the final atomic parameters and R values, we are confident that $P\bar{1}$ is a satisfactory model for refining this structure. In this context, it is worth noting that very similar problems were encountered in the study of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, and that its structure could be refined

Table 1. *High and low values of selected parameters from the $P1$ and $P\bar{1}$ refinements*

		$P1$		$P\bar{1}$	
Parameter		Low	High	Low	High
Distances	C–Cl	1·721 Å	1·760 Å	1·743 Å	(1·743) Å
	C–O	1·320	1·432	1·372	1·396
	C–C	1·315	1·421	1·357	1·389
	C–H	0·659	1·094	0·914	1·008
B	Cl	2·9 Å^{-2}	5·6 Å^{-2}	3·9 Å^{-2}	(3·9) Å^{-2}
	O	3·7	3·8	3·6	(3·6)
	C	2·8	3·7	2·9	3·5
	H	<0	12·6	3·5	5·3

Table 2. *Observed and calculated structure factors in* e *and scaled by a factor of* 48·12

H	K	FOBS	FCAL
** L = 0 **			
1	0	451	416
2	0	182	176
3	0	106	98
4	0	67	10
0	1	870	852
1	-1	2627	2670
1	1	290	302
2	-1	760	743
3	-1	203	177
3	1	80	77
4	1	73	71
4	-1	77	55
0	2	892	882
1	-2	823	783
1	2	227	218
2	2	353	358
2	-2	320	311
3	-2	363	369
3	2	248	262
4	2	157	160
4	-2	206	203
0	3	207	218
1	-3	1427	1387
1	3	543	548
2	3	397	396
2	-3	363	345
3	-3	134	124
3	3	177	180
4	3	177	158
4	-3	87	56
0	4	445	446
1	-4	231	259
1	4	522	517
2	4	238	222
2	-4	618	616
3	-4	170	158
3	4	149	107
4	-4	77	31
0	5	363	379
1	-5	319	324
1	5	92	64
2	5	155	151
2	-5	282	283
3	-5	153	157
3	5	212	201
4	-5	134	108
0	6	114	120
1	-6	65	53
1	6	218	222
2	6	131	113
2	-6	279	290
3	-6	129	124
4	-6	71	57
0	7	179	182
1	-7	71	52
1	7	204	180
2	7	157	156
2	-7	279	297
3	-7	183	168
0	8	143	157
1	-8	153	158
2	-8	95	56
** L = 1 **			
0	0	410	394
-1	-0	139	132
1	0	3668	3759
2	0	63	62
-2	-0	92	90
-3	-0	108	81
3	0	163	146
4	0	76	68
0	1	1883	1946
-0	-1	104	106
1	-1	1778	1704
-1	1	1394	1376
1	1	590	603
-1	-1	291	307
-2	-1	314	333
2	1	173	172
-2	1	479	462
2	-1	1735	1699
3	-1	290	293
-3	1	73	10
-3	-1	214	227
-4	-1	329	353
-0	-2	641	634
0	2	1734	1751
-1	2	501	486
1	-2	542	519
-1	-2	808	832
1	2	629	598
2	2	69	11
-2	-2	477	495
2	-2	325	298
-2	2	637	633
-3	2	421	425
3	-2	210	213
-3	-2	415	437
3	2	97	61
4	2	97	92
4	-2	182	192
-4	2	188	161
0	3	1050	1013
-0	-3	882	897
1	-3	303	307
-1	3	630	614
1	3	110	93
-1	-3	560	545
-2	-3	276	292
2	3	209	210
-2	3	410	392
2	-3	948	912
3	-3	66	35
-3	3	235	253
3	3	187	173
-3	-3	146	134
-4	-3	171	159
4	3	127	99
-4	3	155	151
-0	-4	529	514
0	4	321	357
-1	4	397	384
1	-4	454	452
-1	-4	132	127
1	4	307	307
2	4	298	305
-2	-4	131	131
2	-4	69	77
-2	4	207	213
-3	4	102	92
3	-4	498	499
-3	-4	504	515
3	4	183	181
4	-4	99	89
-4	4	129	122
0	5	408	417
-0	-5	97	96
1	-5	274	281
-1	5	417	420
1	5	277	288
-1	-5	263	269
-2	-5	563	565
2	5	104	97
-2	5	156	144
2	-5	213	208
-3	5	139	131
3	5	97	44
-3	-5	128	106
-4	5	102	98
4	-5	105	116
-0	-6	399	415
0	6	83	76
-1	6	475	507
1	-6	237	244
-1	-6	257	258
-2	-6	114	114
2	-6	91	49
-2	6	170	185
-3	6	153	135
3	-6	129	129
0	7	72	25
-0	-7	185	177
1	-7	223	228
-1	7	241	266
1	7	113	90
-1	-7	255	247
-2	-7	126	106
-2	7	274	283
2	-7	145	129
3	-7	210	213
-3	7	111	89
-0	-8	88	61
0	8	134	104
-1	8	146	129
1	-8	142	149
-1	-8	127	111
2	-8	134	127
-2	8	74	71
** L = 2 **			
0	0	516	510
-1	-0	714	692
1	0	52	30
2	0	1247	1204
-2	-0	284	294
-3	-0	255	277
3	0	113	80
4	0	93	66
-4	-0	235	246
0	1	1183	1184
-0	-1	625	617
1	-1	303	314
-1	1	694	689
1	1	594	592
-1	-1	626	664
-2	-1	493	553
2	1	694	680
-2	1	171	168
2	-1	1106	1047
3	-1	769	788
-3	1	317	313
3	1	84	73
-3	-1	590	640
4	1	86	13
-4	1	63	28
4	-1	102	88
-0	-2	982	977
0	2	617	612
-1	2	859	839
1	-2	671	658
-1	-2	748	779
1	2	1300	1287
2	2	223	221
-2	-2	838	859
2	-2	151	155
-2	2	505	499
-3	2	365	343
3	-2	532	537
-3	-2	238	244
3	2	74	43
4	-2	140	138
-4	2	232	242
0	3	487	495
-0	-3	499	489
1	-3	714	713
-1	3	754	733
1	3	330	298
-1	-3	413	412
-2	-3	218	208
-2	3	574	582
2	-3	277	273
3	-3	365	358
-3	3	242	238
3	3	64	58
-3	-3	215	217
-4	-3	125	117
-4	3	235	220
4	-3	95	105
-0	-4	59	39
-1	4	164	162
1	-4	224	224
-1	-4	69	52
1	4	204	211
2	4	191	178
-2	-4	838	853
2	-4	266	268
-2	4	231	228
-3	4	271	275
-3	-4	75	41
3	4	144	123
4	-4	248	248
-4	4	283	274
0	5	268	261
-0	-5	333	344
1	-5	221	221
-1	5	127	116
1	5	399	409
-1	-5	1044	1054
-2	-5	220	230
2	5	129	140
-2	5	102	65
2	-5	72	81
3	-5	97	107
-3	5	76	56
-3	-5	151	149
-4	5	84	54
4	-5	88	71
-0	-6	440	452
0	6	529	563
-1	6	137	141
1	-6	435	462
-1	-6	97	77
1	6	65	66
-2	-6	149	153
2	-6	229	238
-2	6	195	199
3	-6	66	56
4	-6	71	65
-4	6	101	16
0	7	96	100
-0	-7	205	194
1	-7	121	114
-1	7	291	303
1	7	85	25
-1	-7	150	144
-2	-7	86	24
-2	7	139	135
2	-7	179	197
3	-7	125	124
-3	7	115	86
-0	-8	246	244
0	8	229	187
-1	8	124	84
-1	-8	67	41
2	-8	92	84
-2	8	83	38
** L = 3 **			
0	0	1150	1150
-1	-0	759	753
1	0	405	394
2	0	52	30
-2	-0	630	631
-3	-0	331	338
3	0	296	298
-4	-0	174	187
0	1	327	336
-0	-1	686	691
1	-1	593	590
-1	1	272	268
1	1	469	457
-1	-1	972	985
-2	-1	763	757
2	1	140	133
-2	1	1028	979
2	-1	368	371
3	-1	483	487
-3	1	111	120
3	1	390	391
-4	-1	85	85
-4	1	183	172
4	-1	271	302
-0	-2	759	766
0	2	634	640
-1	2	233	232
1	-2	582	589
-1	-2	1177	1145
1	2	496	491
2	2	602	603
-2	-2	680	686
2	-2	337	337
-2	2	508	486
-3	2	567	547
3	-2	94	51
-3	-2	133	141
3	2	88	77
4	2	76	40
-4	-2	115	101
4	-2	381	382
0	3	733	744
-0	-3	391	362
1	-3	266	277
-1	3	702	724
1	3	252	255
-1	-3	1022	977
-2	-3	223	238
-2	3	364	362
2	-3	273	286
3	-3	161	157
-3	3	170	163
3	3	66	54
-3	-3	280	303
-4	-3	174	149
-4	3	72	64
-0	-4	462	452
-1	4	332	330
1	-4	177	171
-1	-4	954	950
1	4	79	105
2	4	58	14
-2	-4	223	233
2	-4	70	36
-2	4	333	335
-3	4	614	621
3	-4	65	73
-3	-4	123	119
3	4	81	88
-4	4	110	96
0	5	83	85
-0	-5	1211	1229
1	-5	317	354
-1	5	116	86
1	5	82	27
-1	-5	339	353
-2	-5	208	198
2	5	303	284
-2	5	80	75
2	-5	215	207
3	-5	63	15
-3	5	108	81
-3	-5	68	73
-4	5	442	450
4	-5	65	41
-0	-6	402	425
0	6	70	69
-1	6	158	172
1	-6	504	520
-1	-6	245	253
1	6	367	389
2	-6	328	352
3	-6	123	137
-3	-6	122	96
-4	6	111	91
0	7	193	188
-0	-7	81	89
1	-7	59	36
-1	7	148	156
-1	-7	106	78
-2	-7	181	149
-2	7	101	104
2	-7	83	43
3	-7	128	133
-3	7	83	43
-0	-8	73	22
-1	8	108	33
1	-8	291	281
-1	-8	200	183
2	-8	66	8
** L = 4 **			
0	0	1069	1067
-1	-0	544	561
1	0	780	775
2	0	244	230
-2	-0	392	391
-3	-0	241	250
-4	-0	71	65
0	1	189	194
-0	-1	878	868
1	-1	361	376
-1	1	1805	1731
-1	-1	404	406
-2	-1	86	111
2	1	77	52
-2	1	74	98
2	-1	344	337
3	-1	247	248
-3	1	348	346
3	1	89	25
-3	-1	245	260
-4	-1	225	241
4	1	156	170
-4	1	145	163
4	-1	193	189
-0	-2	718	661
0	2	67	56
-1	2	253	241
1	-2	393	398
-1	-2	1079	1037
1	2	261	259
2	2	297	282
-2	-2	441	454
2	-2	234	232
-2	2	912	855
-3	2	160	153
3	-2	105	81
-3	-2	281	303
3	2	227	224
-4	-2	172	168
4	-2	92	20
-4	2	142	138
0	3	491	498
-0	-3	1598	1523
1	-3	144	125
-1	3	520	513
1	3	416	419
-1	-3	213	229
-2	-3	507	534
2	3	131	133
-2	3	229	225
2	-3	86	102
3	-3	79	69
-3	-3	264	282
-4	-3	69	58
-4	3	122	95
-0	-4	586	601
0	4	234	258
-1	4	229	239
1	-4	683	684
-1	-4	466	456
1	4	153	159
2	4	64	63
-2	-4	171	173
2	-4	218	200
-2	4	952	972
-3	4	318	294
3	4	98	66
-4	-4	103	34
-4	4	71	16
0	5	146	168
-0	-5	318	325
1	-5	838	859
-1	5	163	170
1	5	73	24
-1	-5	114	124
-2	-5	62	50
2	5	77	69
-2	5	60	46
2	-5	246	276
3	-5	148	139
-3	5	588	613
-3	-5	90	89
-4	5	82	10
-0	-6	232	243
1	-6	585	615
-1	-6	142	147
1	6	63	35
-2	-6	249	232
2	-6	366	377
-3	6	83	64
3	-6	184	198
-3	-6	165	158
0	7	120	128
-0	-7	196	201
-1	-7	279	270
-2	-7	185	180
2	-7	229	239
3	-7	83	3
-3	7	141	119
-0	-8	225	219
1	-8	64	44
-1	-8	164	145
2	-8	191	167
** L = 5 **			
0	0	95	48
-1	-0	449	424
1	0	816	820
2	0	369	362
-2	-0	160	156
3	0	115	88
4	0	66	35
-4	-0	188	197
0	1	1496	1480
1	-1	246	256
-1	1	114	61
1	1	170	163
-2	-1	537	528
2	1	121	106
-2	1	487	492
2	-1	152	174
3	-1	142	147
-3	1	191	196
3	1	98	58
-3	-1	503	523
-4	-1	257	260
-4	1	71	40
4	-1	110	100
-0	-2	842	806
0	2	260	262
-1	2	772	747
1	-2	84	44
-1	-2	890	865
1	2	97	95
2	2	104	77
-2	-2	533	557
2	-2	102	103
-2	2	300	309
-3	2	285	293
3	-2	68	66
-3	-2	219	235
3	2	94	97
-4	-2	110	95
4	-2	65	22
-4	2	176	175
0	3	508	505
-0	-3	254	267
1	-3	1167	1160
-1	3	756	751
1	3	259	248
-1	-3	589	596
-2	-3	261	284
2	3	125	121
-2	3	58	32
2	-3	65	36
3	-3	72	19
-3	3	221	213
3	3	70	63
-3	-3	96	92
-4	-3	132	152
-4	3	136	130
-0	-4	476	475
0	4	126	105
-1	4	948	978
1	-4	117	144
-1	-4	65	85
1	4	126	122
2	4	132	123
-2	-4	154	159
2	-4	536	558
-2	4	506	504
3	-4	135	134
-3	-4	194	192
4	-4	83	23
0	5	141	155
-0	-5	74	72
1	-5	187	189
-1	5	89	87
1	5	127	119
-1	-5	265	270
-2	-5	198	194
-2	5	502	522
2	-5	330	342
3	-5	134	157
-3	5	94	50
-3	-5	199	195
-4	5	117	52
-0	-6	247	244
0	6	93	84
1	-6	115	105
-1	-6	312	310
1	6	66	24
-2	-6	283	280
2	-6	506	510
-2	6	271	279
-3	6	91	72
3	-6	207	182
-0	-7	292	303
1	-7	224	233
-1	7	105	33
-1	-7	215	200
-2	-7	155	117
-2	7	122	120
2	-7	121	128
3	-7	269	265
-0	-8	110	103
1	-8	164	170
2	-8	71	81
** L = 6 **			
0	0	316	298
-1	-0	96	99
1	0	312	287
2	0	424	431
-2	-0	315	306
-3	-0	330	326
3	0	151	142
-4	-0	491	508
0	1	79	47
-0	-1	196	199
1	-1	53	45
-1	1	423	421
1	1	693	698
-1	-1	718	685
-2	-1	725	724
2	1	168	149
-2	1	78	72
2	-1	121	109
3	-1	97	67
-3	1	88	74
3	1	107	66
-3	-1	548	550
-4	-1	204	211
-4	1	114	125
-0	-2	870	863
0	2	286	284
-1	2	403	408
1	-2	417	425
-1	-2	665	668
1	2	467	477
2	2	75	56
-2	-2	241	249
2	-2	98	75
-2	2	349	364
-3	2	168	169
-4	2	92	81
0	3	854	899
-0	-3	331	354
1	-3	255	269
1	3	351	349
-1	-3	105	99
-2	-3	90	48
2	3	131	95
-2	3	315	321
2	-3	576	591
-3	3	202	220
-3	-3	321	340
-4	-3	82	30
-4	3	118	132
-0	-4	83	76
0	4	982	999
-1	4	467	491
1	-4	226	237
-1	-4	258	269
-2	-4	465	482
2	-4	86	63
-2	4	156	147
-3	4	150	134
3	-4	294	310
-3	-4	105	70
-4	4	84	80
0	5	192	174
-0	-5	368	388
1	-5	194	196
-1	5	216	212
1	5	121	83
-1	-5	319	317
-2	-5	280	265
-2	5	95	95
2	-5	84	77
3	-5	85	44
-3	5	88	80
-3	-5	193	213
-4	5	102	84
-0	-6	270	267
0	6	64	24
-1	6	349	363
1	-6	208	220
-1	-6	339	337
-2	-6	164	143
2	-6	68	18
-3	6	71	91
3	-6	275	287
-0	-7	166	165
1	-7	216	223
-1	7	92	55
-1	-7	83	55
-2	-7	246	211
2	-7	124	148
** L = 7 **			
0	0	241	251
-1	-0	447	442
1	0	93	95
2	0	230	224
-2	-0	463	463
-3	-0	652	656
3	0	165	151
-4	-0	88	81
0	1	159	161
-0	-1	533	542
1	-1	248	256
-1	1	136	123
-1	-1	653	655
-2	-1	775	784
2	1	171	171
-2	1	189	179
3	-1	168	158
-3	1	395	400
3	1	101	102
-3	-1	478	486
-4	-1	111	117
-4	1	189	190
-0	-2	499	511
0	2	296	332
-1	2	241	240
1	-2	468	490
-1	-2	215	208
2	2	397	395
-2	-2	433	438
2	-2	213	226
-2	2	86	81
-3	2	61	56
-3	-2	68	60
-4	-2	137	133
-4	2	303	288
0	3	59	24
-0	-3	123	118
1	-3	117	107
-1	3	281	294
1	3	598	631
-1	-3	164	161
-2	-3	460	474
2	3	188	185
-2	3	180	194
2	-3	162	161
3	-3	227	239
-3	3	163	159
-3	-3	161	164
-4	-3	184	175
-4	3	128	129
-0	-4	285	291
0	4	269	280
-1	4	233	236
1	-4	132	139
-1	-4	685	704
1	4	223	212
2	4	76	5
-2	-4	119	82
-2	4	220	216
-3	4	139	108
3	-4	106	80
-3	-4	271	293
-4	4	79	72
0	5	87	39
-0	-5	362	373
1	-5	326	325
-1	5	73	85
1	5	179	158
-1	-5	203	166
-2	-5	233	263
-2	5	93	100
2	-5	160	153
3	-5	81	33
-3	5	164	152
-3	-5	65	45
-0	-6	236	231
0	6	259	265
1	-6	157	158
-1	-6	100	70
-2	-6	76	84
2	-6	124	124
-2	6	99	32
3	-6	67	33
-0	-7	78	52
1	-7	83	91
-1	-7	289	267
2	-7	105	115
-0	-8	328	300
1	-8	140	92
** L = 8 **			
0	0	340	359
-1	-0	513	521
1	0	192	188
2	0	74	15
-2	-0	471	477
3	0	111	99
0	1	141	168
-0	-1	401	400
1	-1	272	294
-1	1	231	225
-1	-1	664	667
-2	-1	733	724
2	1	65	42
-2	1	637	664
2	-1	146	150
-3	1	118	103
-4	-1	69	68
-4	1	150	166
-0	-2	131	116
0	2	108	69
-1	2	57	7
1	-2	266	277
-1	-2	890	881
1	2	135	149
2	2	126	119
-2	-2	138	157
2	-2	166	178
-2	2	85	50
-3	2	447	464
3	-2	103	102
-3	-2	296	302
-4	-2	196	202
-4	2	100	89
0	3	161	145
-0	-3	383	390
1	-3	215	209
-1	3	89	86
-1	-3	344	329
-2	-3	340	342
2	3	297	301
-2	3	128	132
2	-3	73	22
3	-3	81	51
-3	-3	276	279
-4	3	122	125
-0	-4	581	592
0	4	201	205
-1	4	206	206
1	-4	236	229
-1	-4	87	59
1	4	97	96
-2	-4	314	338
2	-4	136	116
-2	4	99	109
-3	4	71	62
-3	-4	75	72
-0	-5	64	40
1	-5	273	283
-1	5	104	82
-1	-5	246	251
-2	5	156	155
2	-5	202	189
3	-5	71	61
-3	5	221	199
-3	-5	168	158
-1	-6	157	160
-2	-6	288	267
2	-6	94	61
-0	-7	260	254
1	-7	92	88
-1	-7	225	213
** L = 9 **			
0	0	379	407
-1	-0	104	76
1	0	217	213
2	0	74	66
-2	-0	66	71
-3	-0	161	159
-4	-0	156	144
0	1	188	197
-0	-1	282	287
1	-1	183	171
-1	1	604	647
1	1	88	101
-1	-1	647	647
-2	-1	110	124
2	-1	121	129
-3	1	165	176
-3	-1	196	192
-4	-1	143	150
-0	-2	910	919
0	2	91	36
-1	2	159	145
-1	-2	210	201
2	2	75	21
-2	-2	408	414
2	-2	121	110
-2	2	445	464
-3	2	180	170
-3	-2	291	290
-4	-2	143	142
-4	2	103	61
1	-3	407	422
-1	-3	432	447
-2	-3	268	280
-2	3	72	77
2	-3	176	171
-3	3	126	132
-3	-3	122	93
-0	-4	96	66
0	4	148	133
-1	4	130	100
1	-4	248	253
-1	-4	223	235
1	4	116	97
-2	-4	72	42
2	-4	103	129
-3	4	82	20
-3	-4	169	159
-0	-5	165	169
1	-5	123	137
-1	5	99	95
-1	-5	184	174
-2	-5	277	273
-2	5	254	245
2	-5	137	131
-0	-6	208	215
-1	-6	322	325
-2	-6	282	233
2	-6	83	63
-0	-7	223	217
1	-7	185	196
-1	-7	161	144
** L = 10 **			
0	0	159	175
-1	-0	101	79
1	0	230	221
2	0	104	97
-2	-0	224	242
-3	-0	278	267
0	1	376	405
-0	-1	343	351
1	1	107	109
-1	-1	263	271
-2	-1	283	277
2	1	67	43
-2	1	86	72
2	-1	103	67
-3	-1	157	168
-0	-2	144	126
0	2	129	133
-1	2	294	297
1	-2	565	591
-1	-2	330	343
1	2	80	43
-2	-2	235	251
-2	2	222	218
-3	2	86	42
-3	-2	166	145
0	3	93	49
-0	-3	367	373
1	-3	194	203
-1	3	102	98
-1	-3	167	165
-2	3	131	117
2	-3	285	293
-3	3	195	201
-3	-3	158	131
-0	-4	64	60
0	4	126	78
-1	4	150	139
1	-4	110	99
-1	-4	152	150
-2	-4	277	255
-3	-4	276	268
-0	-5	233	214
1	-5	68	64
-1	-5	297	335
-2	-5	263	262
2	-5	113	93
-0	-6	255	262
1	-6	189	188
-1	-6	242	198
** L = 11 **			
0	0	85	24
-1	-0	201	220
1	0	183	191
-2	-0	288	283
-3	-0	228	226
-0	-1	239	250
1	-1	111	115
-1	1	73	58
1	1	194	178
-1	-1	265	247
-2	-1	139	127
-2	1	104	101
-3	1	149	121
-3	-1	114	70
-0	-2	166	165
0	2	128	132
-1	2	180	171
-1	-2	112	115
2	-2	245	259
-2	2	79	4
-3	2	106	78
-3	-2	113	87
0	3	67	30
-0	-3	65	50
1	-3	207	195
-1	3	118	102
-1	-3	88	70
-2	-3	221	232
-2	3	145	148
-3	-3	317	311
-0	-4	172	162
-1	-4	293	282
-2	-4	377	340
-0	-5	247	242
1	-5	175	146
-1	-5	230	231
-2	-5	91	75
-0	-6	124	108
** L = 12 **			
0	0	135	122
-1	-0	203	192
-2	-0	241	240
0	1	93	94
-0	-1	175	151
1	-1	141	127
-1	1	155	128
-1	-1	67	70
-2	-1	68	65
-2	1	120	125
1	-2	74	61
-1	-2	63	12
-2	-2	163	140
-2	2	128	106
-0	-3	105	84
-1	-3	253	251
-2	-3	317	309
-0	-4	231	219
-1	-4	308	293
** L = 13 **			
-1	-0	151	149
-1	-1	173	164
-0	-2	98	71
-1	-2	93	94
-1	-3	230	217

to a very respectable R_1 of 3·6% in the centric space group. The results of the above calculations suggest that judgement should be exercised in accepting the results of R value ratio tests when the matrix equations are not well-behaved, as, for example, in the vicinity of symmetry elements not explicitly incorporated in the normal equations, and that intensity statistics may often be the preferred method for distinguishing between two space groups.

Full-matrix least-squares refinement was then continued, assuming anisotropic thermal parameters for the Cl, O, and C atoms, and introducing a dispersion correction for Cl. The final R values were $R_1=0·057$ and $R_2=0·062$. That reasonable convergence was attained is indicated by the values $(\Delta/\sigma)_{\max}=0·05$ for nonhydrogen atoms and 0·33 for hydrogen atoms. A final difference Fourier showed no positive peaks greater than 0·34 e.Å^{-3} and no negative regions below $-0·41$ e.Å^{-3}. The largest negative peak occurred at the origin.

Observed and calculated structure factors are given in Table 2, and the final atomic parameters and their standard deviations, as calculated in the last least-squares cycle, are listed in Table 3. Intramolecular distances and angles are summarized in Table 4, and the amplitudes and directions of anisotropic thermal motion are listed in Table 5 and displayed in the form of 50% probability thermal ellipsoids in Fig. 1. The standard deviations in Tables 4 and 5 were computed from the variance–covariance matrix obtained in the last least-squares cycle.

Table 4. *Bond distances and angles in* 2,7-*dichlorodibenzo-p-dioxin*

Distances (Å)

Cl—C(6)	1·742 (4)	C(3)–C(5)	1·378 (5)
O—C(1)	1·382 (4)	C(4)–C(6)	1·386 (5)
O′—C(2)	1·380 (4)	C(5)–C(6)	1·378 (5)
C(1)–C(2)	1·397 (5)	C(3)–H(3)	0·96 (3)
C(1)–C(3)	1·373 (5)	C(4)–H(4)	0·93 (4)
C(2)–C(4)	1·370 (5)	C(5)–H(5)	0·88 (3)

Table 3. *Atomic parameters for* 2,7-*dichlorodibenzo-p-dioxin*

	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cl	−0·4292 (3)	−0·3654 (1)	0·3777 (1)	945 (9)	240 (2)	106 (1)	85 (3)	142 (2)	63 (1)
O	0·0466 (7)	0·2155 (3)	0·0479 (2)	1110 (25)	134 (5)	72 (2)	82 (8)	114 (6)	15 (3)
C(1)	−0·0668 (8)	0·0749 (5)	0·1228 (3)	587 (26)	159 (7)	66 (3)	74 (11)	36 (7)	30 (4)
C(2)	−0·1125 (8)	−0·1359 (5)	0·0757 (3)	569 (26)	165 (2)	66 (3)	77 (11)	35 (7)	21 (4)
C(3)	−0·1340 (9)	0·1467 (5)	0·2468 (3)	694 (29)	166 (8)	78 (4)	74 (12)	64 (8)	3 (4)
C(4)	−0·2219 (9)	−0·2706 (5)	0·1534 (3)	599 (28)	160 (9)	84 (4)	63 (11)	41 (8)	32 (4)
C(5)	−0·2452 (9)	0·0123 (5)	0·3255 (3)	640 (29)	213 (9)	77 (4)	110 (12)	84 (8)	25 (5)
C(6)	−0·2894 (8)	−0·1955 (5)	0·2782 (3)	453 (24)	208 (8)	89 (4)	89 (11)	55 (7)	58 (4)
				B					
H(3)	−0·094 (4)	0·293 (5)	0·278 (3)	3·5 (8)					
H(4)	−0·240 (9)	−0·411 (6)	0·124 (4)	4·4 (9)					
H(5)	−0·283 (9)	0·058 (5)	0·406 (4)	4·0 (9)					

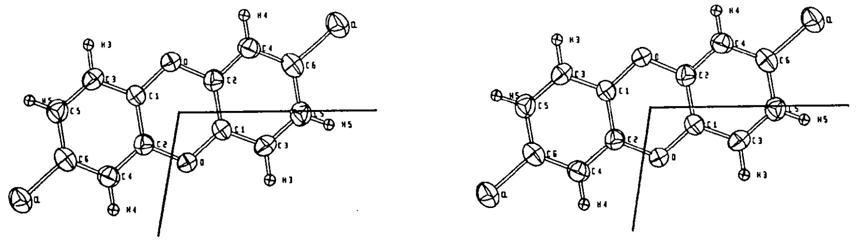

Fig. 1. Stereoscopic view of a molecule of 2,7-dichlorobenzo-*p*-dioxin showing the ellipsoids of thermal motion and indicating the numbering system.

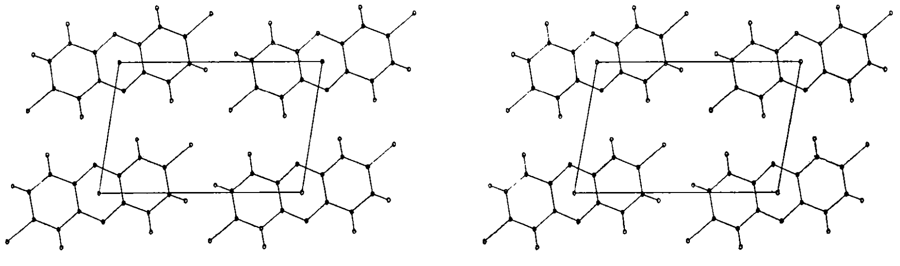

Fig. 2. Stereoscopic view of molecular packing in the *yz* plane of 2,7-dichlorodibenzo-*p*-dioxin. The unit cell outline in this plane is drawn.

Table 4 (*cont.*)

Angles (°) Vertex	Atom 1	Atom 2		Vertex	Atom 1	Atom 2	
O	C(1)	C(2′)	116·3 (2)				
C(1)	O	C(2)	121·7 (3)	C(2)	O′	C(1)	122·0 (3)
	O	C(3)	118·5 (3)		O′	C(4)	118·0 (3)
	C(2)	C(3)	119·8 (3)		C(1)	C(4)	120·1 (3)
C(3)	C(1)	C(5)	120·6 (3)	C(4)	C(2)	C(6)	119·4 (3)
	C(1)	H(3)	118 (2)		C(2)	H(4)	120 (2)
	C(5)	H(3)	121 (2)		C(6)	H(4)	121 (2)
C(5)	C(3)	C(6)	119·2 (3)	C(6)	C(4)	C(5)	121·0 (3)
	C(3)	H(5)	121 (2)		C(4)	Cl	119·7 (3)
	C(6)	H(5)	120 (2)		C(5)	Cl	119·3 (3)

* Primed atoms are related by the center at (0,0,0). Errors in parentheses are referred to the last significant digit cited.

Table 5. *R.m.s. amplitudes of thermal motion along the principal axes**

	Axis 1	Axis 2	Axis 3
Cl	0·1831 (12)	0·2375 (12)	0·2691 (13)
O	0·166 (3)	0·181 (3)	0·282 (3)
C(1)	0·171 (4)	0·190 (4)	0·205 (4)
C(2)	0·181 (4)	0·186 (4)	0·203 (4)
C(3)	0·173 (5)	0·212 (4)	0·223 (5)
C(4)	0·181 (4)	0·202 (5)	0·210 (5)
C(5)	0·179 (5)	0·210 (4)	0·222 (5)
C(6)	0·174 (5)	0·180 (4)	0·229 (4)

* Ordered on increasing magnitude.

The atomic scattering factors for Cl, C, and O were taken from the *International Tables for X-ray Crystallography* (1962). The scattering factor for hydrogen is that calculated by Stewart, Davidson & Simpson (1965). Fourier summations, least-squares refinements, and error analysis were based on adaptations of standard programs by Gvildys (1964, 1965*a*, *b*, 1967), and illustrations were prepared using a local version of the thermal ellipsoid plot program of Johnson (1965).

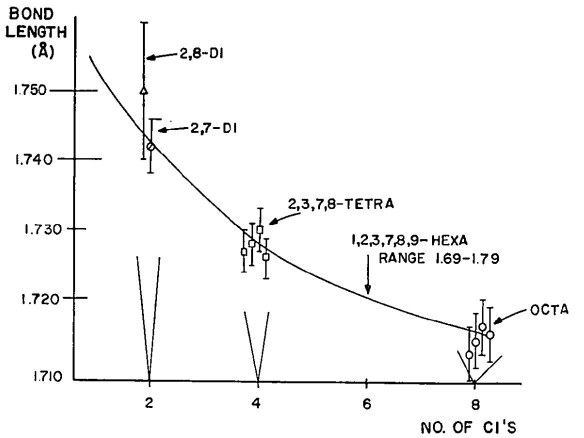

Fig. 3. Carbon–chlorine bond lengths (Å) in chlorinated dibenzo-*p*-dioxins as a function of the degree of chlorine substitution.

Discussion

2,7-Dichlorodibenzo-*p*-dioxin is found to be planar within experimental error; because it is situated on a crystallographic inversion center, the approximate molecular symmetry in the crystal is C_{2h}. For the unique atoms, the calculated (Gvildys, 1965*b*) deviations from the least-squares plane, based on the nonhydrogen atoms, are Cl, 0·005; O, 0·003; C(1), −0·004; C(2), −0·008; C(3), −0·002; C(4), −0·001; C(5), 0·001; C(6), −0·002; H(3), 0·024; H(4), 0·042; and H(5), 0·025 (Å). Deviations for the 11 atoms related by the center are, of course, equal but opposite in sign. The equation of the plane is $3{\cdot}489x-1{\cdot}338y+2{\cdot}682z=0$.

The crystal contains only one unusually short intermolecular interaction: the Cl···Cl contact of 3·402 Å across the inversion center at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. This distance is approximately 0·2 Å less than the sum of two chlorine van der Waals radii (3·6 Å), and, interestingly, is comparable to several short Cl···Cl intermolecular distances (3·44, 3·46, 3·47 Å) occurring in 1,2,3,7,8,9-hexachlorodibenzo-*p*-dioxin (Cantrell, *et al.*, 1969). The only other nonhydrogen contacts below 3·6 Å in the crystal occur between molecules stacked in the short (3·878 Å) cell translation along *x*. Distances between atoms related directly by this translation are C(4)···C(6), 3·526; C(1)···C(3), 3·528; O···C(3), 3·591; C(2)···C(6), 3·596; and C(1)···C(5), 3·600 (Å); whereas those based on the inversion center at $(\frac{1}{2},0,0)$ are O···C(2), 3·527; C(1)···C(2), 3·575; and O···C(4) 3·585 (Å). The perpendicular distance between planes related by the lattice period along *x* is 3·489 Å; the normal to the molecular plane forms an angle of 25·9° with the *x* axis. A view of the molecular packing in the *yz* planes is given in Fig. 2.

The C–Cl bond, 1·742 ± 0·004 Å, is within experimental error of the value (Fig. 3) determined for 2,8-dichlorodibenzo-*p*-dioxin (Boer, Neuman & Aniline, 1972). It is 3–4 standard deviations longer than the C–Cl bond lengths determined for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and 6–7 standard deviations longer than C–Cl bonds in octachlorodibenzo-*p*-dioxin (Neuman, North & Boer, 1972). These results reveal an interesting trend toward bond shortening with increasing chlorine substitution on the rings. The accuracy and internal agreement of the data are such as to suggest that these differences are real; they also persist when the bond distances are corrected assuming rigid-body thermal motion (Schomaker & Trueblood 1968). We attribute this effect to a reduction in the effective electronegativity difference between C and Cl atoms as more electron density is withdrawn from the aromatic ring upon increased substitution; as a result, the C–Cl bonds have increased covalent character and exhibit shorter distances.

Other bond distances and angles are quite regular. The C–O distances of 1·380 and 1·382 (±0·004) Å are very close to the average value of 1·378 Å in TCBD. Similarly, the C–C distances, which range between 1·370 and 1·397 (±0·005) Å, vary by no more than 0·01 Å from values for the corresponding ring positions in TCBD. The C–H distances of 0·88, 0·93, and 0·96 Å are subject both to larger random errors and to systematic shortening from the true internuclear separation, due to the attraction of electron density from the hydrogen nucleus toward the bonding region (Stewart *et al.*, 1965). The C–O–C angle in the central ring is 116.3 ± 0·2° (compare 115·6° and 115·8° in TCBD), while the corresponding C–C–O angles in the heterocycle are 121·7 and 122·0°. The angle of 121·0 ± 0·3° at C(6) might be significantly different (3σ) from 120°; if so, the increased angle could also be accounted for by rehybridization resulting from withdrawal of *p*-character from carbon by the more electronegative chlorine atom (Bent, 1961). Bond angles at the remaining carbon atoms are indistinguishable from the trigonal angle within the accuracy of this experiment.

That the chlorine and oxygen atoms display the most thermal anisotropy can be seen from Table 5. For the chlorine, the largest thermal amplitude is in the molecular plane in a direction perpendicular to the C–Cl bond (Fig. 1), whereas for the oxygen the largest vibrational component forms an angle of 18·0 ± 1·3° with the x axis and is thus roughly orthogonal to the plane of the molecule.

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