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The Crystal Structure of 2-Chlorobiphenyl-4-carboxylic Acid

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The crystal structure of 2-chlorobiphenyl-4-carboxylic acid ($C_{13}H_9O_2Cl$) has been determined from three-dimensional X-ray diffraction data by Patterson methods. The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions: $a=3{\cdot}896$, $b=9{\cdot}549$, $c=14{\cdot}184$ Å; $\alpha=92{\cdot}01°$, $\beta=95{\cdot}99°$, $\gamma=92{\cdot}44°$.

The structure was refined using anisotropic thermal parameters to a residual of 13% for the 1425 observed structure factors. The crystal structure consists of centrosymmetrical hydrogen-bonded dimers, the molecules being separated by approximately 4 Å perpendicular to the ring planes. The angle between the planes of the phenyl rings of each molecule is 46·1° and that between the carboxyl group and the phenyl ring to which it is attached 7·9°.

Introduction

This paper describes an X-ray crystallographic study of 2-chlorobiphenyl-4-carboxylic acid, the third in a series of structure determinations of halogen-substituted biphenyls selected for study because of the lack of data available on the solid states of compounds exhibiting liquid crystalline phases (Gray, Sutherland & Young, 1965).

Experimental

Crystal data

$C_{13}H_8O_2Cl$, $M=232{\cdot}7$. Triclinic;

$a=3{\cdot}896\pm0{\cdot}003$, $b=9{\cdot}549\pm0{\cdot}005$, $c=14{\cdot}184\pm0{\cdot}005$ Å
$\alpha=92{\cdot}01\pm0{\cdot}08°$, $\beta=95{\cdot}99\pm0{\cdot}08°$, $\gamma=92{\cdot}44\pm0{\cdot}08°$;
$U=526{\cdot}4$ Å^3; $D_m=1{\cdot}46\pm0{\cdot}01$ g.cm^{-3}, $D_c=1{\cdot}47$ g.cm^{-3}
$Z=2$, $F(000)=240$, Cu $K\alpha(\lambda=1{\cdot}5418$ Å), $\mu=30{\cdot}4$ cm^{-1}.

No absent spectra, space group $P1$ or $P\bar{1}$ uniquely determined as $P\bar{1}$ in the structure analysis.

The quoted cell is related to that described in a publication by Hoy & Sutherland (1966), which was for a left handed set of axes, by the vector transformation 100/010/−10–1.

The observed density at 17°C was measured by the method of flotation using aqueous cadmium n-dodecatungstaborate. Slow evaporation from ethanol produced transparent, colorless, needle shaped crystals which gave sharp extinctions along their needle axes when viewed under a polarizing microscope.

A single crystal having dimensions 0·003 × 0·0015 cm perpendicular to the needle axis was used to collect diffraction data for the 0*kl*, 1*kl*, 2*kl*, 3*kl* and *h*0*l* layers of the reciprocal lattice by the multiple-film Weissenberg method. The intensities were estimated visually by comparison with a calibrated scale and corrected for Lorentz and polarization factors. The Phillips (1954) correction factor was applied to the non-zero-level data. The 0*kl* zone was placed on an approximate absolute scale from a Wilson plot and by means of the *h*0*l* zone, the 0*kl*, 1*kl*, 2*kl* and 3*kl* data were reduced to an approximate absolute scale. No correction was applied for absorption.

The data reduction was carried out on an Elliott 803B computer using the authors' programs.

Structure determination

A two-dimensional sharpened Patterson was computed from the 0*kl* data and is shown in Fig. 1(*a*). This contained three peaks of considerable height, *A*, *B* and *C*, which were possible Cl–Cl vectors; peaks *A* and *C* were eliminated by considering possible positions of the molecule on the assumption that the molecules form hydrogen bonded dimers across a centre of symmetry. Using *B* as the Cl–Cl vector, a minimum function was drawn, Fig. 1(*b*), from which a set of coordinates for the thirteen carbon and two oxygen atoms were extracted. A structure factor calculation from these coordinate gave a residual of $R(0kl)=0{\cdot}45$, where $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ which was reduced by a series of Fourier refinements to 0·20 and by four cycles of least-squares refinement on positional and isotropic thermal parameters to 0·153.

A sharpened Patterson synthesis was calculated from the *h*0*l* data to determine the x coordinates of the atoms [Fig. 2(*a*)]. This showed a prominent peak with a 2 z coordinate corresponding to that obtained for the chlorine from the (yz) synthesis. The minimum function [Fig. 2(*b*)] constructed from this rotation peak, could be interpreted in two ways. The first model gave structure factors with a residual of 0·50 which dropped to 0·29 on refinement: the second had an initial residual of 0·36 which dropped to 0·20 on refinement; it was therefore assumed that the second model was probably the correct one.

Refinement

On the basis of a set of three-dimensional positional parameters, formed from the x coordinates of the *h*0*l* projection and the y and z coordinates of the 0*kl* pro-

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jection, the structure was refined (using the complete three-dimensional data) by three cycles of Fourier refinement from a residual of 0·33 to 0·21.

After scaling $\Sigma|F_o|$ to $\Sigma|F_c|$ for each layer of the reciprocal lattice, refinement was continued by block-diagonal least-squares applied to positional and isotropic thermal parameters and overall scale factor on an Elliott 803B computer using the block-diagonal least-squares program of Daly, Stephens & Wheatley (1963) to a residual $R=0{\cdot}16$. The inclusion of anisotropic thermal parameters of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)]$$

(Cruickshank, 1961) resulted in a residual of $R=0{\cdot}14$.

A three-dimensional difference electron density distribution was calculated; this gave a clear indication of the approximate positions of all the hydrogen atoms.

At this stage the refinement was transferred to the University of Leeds KDF9 computer using the program of Cruickshank & Smith (1966). During the subsequent block-diagonal least-squares refinement ap-

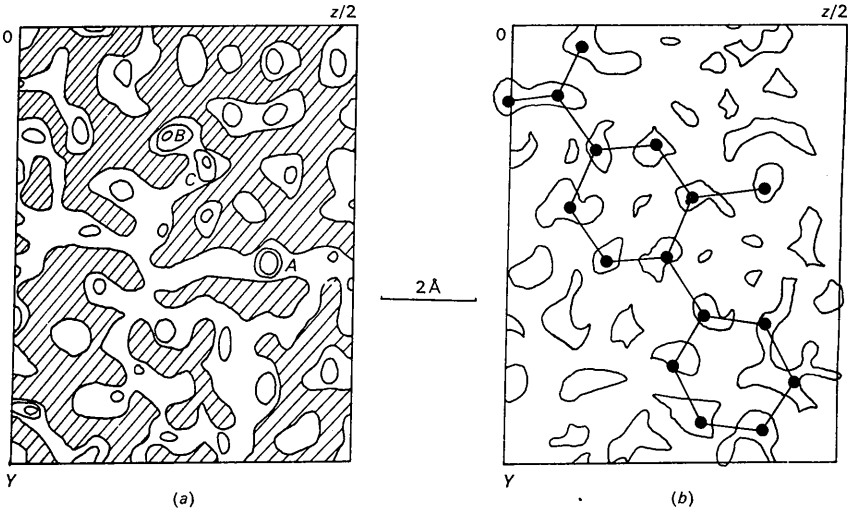

Fig. 1. (*a*) Sharpened Patterson for the (y,z) projection. (*b*) Minimum function for the (y,z) projection.

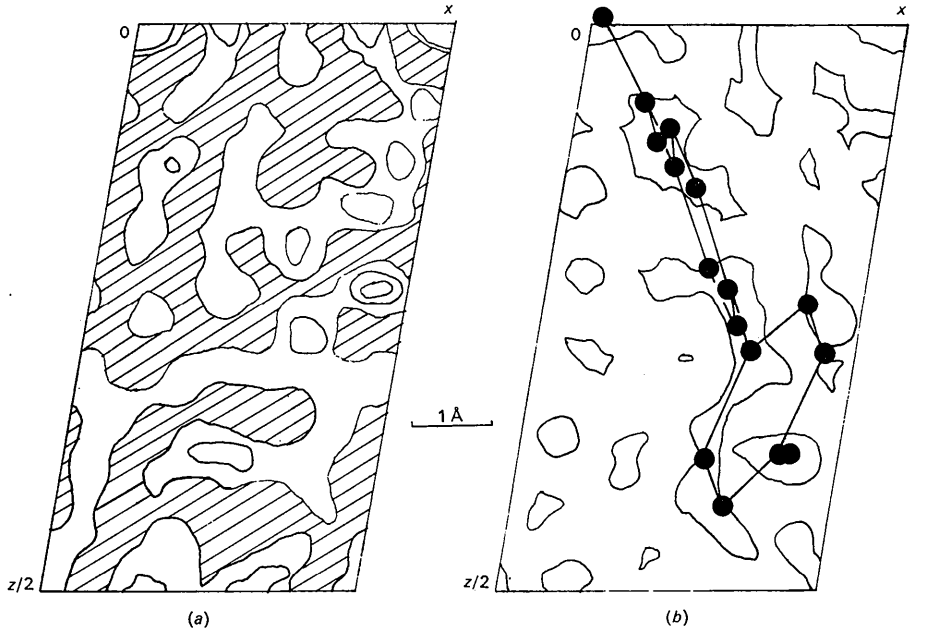

Fig. 2. (*a*) Sharpened Patterson for the (x,z) projection. (*b*) Minimum function for the (x,z) projection.

Table 1. *Observed and calculated structure factors*

The Table is in groups of h, k, l, $100F_o$ and $100F_c$. An asterisk denotes an unobserved reflexion.

0 0 1	*	598	0 4 2	3158 -3207
0 0 2	*	-1844	0 4 -2	1063 865
0 0 3	2550	2572	0 4 3	3116 -3113
0 0 4	2599	-2567	0 4 -3	3422 -3516
0 0 5	1265	1221	0 4 4	3217 3390
0 0 6	3530	-3771	0 4 -4	865 -829
0 0 7	1098	987	0 4 5	709 -714
0 0 8	3585	3571	0 4 -5	848 -874
0 0 9	1132	-999	0 4 6	926 816
0 0 10	1984	1780	0 4 -6	535 -411
0 0 11	703	621	0 4 7	* 201
0 0 12	830	-897	0 4 -7	369 -311
0 0 13	1799	1931	0 4 8	432 311
0 0 14	*	-144	0 4 -8	1218 -1148
0 0 15	*	-151	0 4 9	971 941
0 0 16	624	683	0 4 -9	3238 3326
0 0 17	565	-717	0 4 10	2758 -2895
0 0 18	474	717	0 4 -10	520 345
0 1 0	*	-2111	0 4 11	522 -265
0 1 1	*	931	0 4 -11	1812 -1829
0 1 -1	*	1706	0 4 12	536 533
0 1 2	252	-130	0 4 -12	1079 1105
0 1 -2	4917	5639	0 4 13	780 -844
0 1 3	1819	-1774	0 4 -13	771 -844
0 1 -3	2608	2657	0 4 14	* 336
0 1 4	677	551	0 4 -14	* 106
0 1 -4	1767	1804	0 4 15	* -6
0 1 5	*	-104	0 4 -15	* -215
0 1 -5	2363	-2339	0 4 16	* -113
0 1 6	1064	-1131	0 4 -16	462 -584
0 1 -6	1774	1893	0 4 17	* 262
0 1 7	1847	1691	0 4 -17	634 875
0 1 -7	1169	-972	0 5 0	1273 1350
0 1 8	327	-239	0 5 1	947 955
0 1 -8	2410	-2511	0 5 -1	785 -658
0 1 9	1299	1177	0 5 2	* -15
0 1 -9	1849	1734	0 5 -2	2848 2917
0 1 10	1445	1008	0 5 3	974 805
0 1 -10	*	-224	0 5 -3	886 769
0 1 11	650	-612	0 5 4	459 -345
0 1 -11	1075	1040	0 5 -4	801 609
0 1 12	1183	1024	0 5 5	* 225
0 1 -12	514	274	0 5 -5	931 754
0 1 13	540	-555	0 5 6	901 821
0 1 -13	1138	-1228	0 5 -6	2756 -2721
0 1 14	*	339	0 5 7	835 -710
0 1 -14	*	220	0 5 -7	787 686
0 1 15	*	307	0 5 8	1313 1205
0 1 -15	*	-126	0 5 -8	* -211
0 1 16	477	-540	0 5 9	925 909
0 1 -16	611	681	0 5 -9	1304 -1243
0 1 17	737	886	0 5 10	1011 -923
0 1 -17	403	462	0 5 -10	1493 1262
0 1 18	*	183	0 5 11	771 797
0 1 -18	273	-489	0 5 -11	1575 1492
0 2 0	1108	-837	0 5 12	466 -414
0 2 1	3565	3640	0 5 -12	1576 1687
0 2 -1	2281	-2176	0 5 13	* 15
0 2 2	4059	-4144	0 5 -13	* -93
0 2 -2	3552	3772	0 5 14	* 88
0 2 3	807	661	0 5 -14	660 -750
0 2 -3	2196	-2070	0 5 15	446 -634
0 2 4	2560	-2446	0 5 -15	661 771
0 2 -4	1165	-1049	0 5 16	504 754
0 2 5	2108	-2225	0 5 -16	323 -253
0 2 -5	1804	-1616	0 5 -17	* -754
0 2 6	1083	839	0 6 0	495 429
0 2 -6	1843	-1985	0 6 1	1106 -1086
0 2 7	2143	-2017	0 6 -1	1568 1493
0 2 -7	1807	1561	0 6 2	2136 2348
0 2 8	1167	868	0 6 -2	* 103
0 2 -8	1169	-912	0 6 3	639 -514
0 2 9	417	221	0 6 -3	1854 1735
0 2 -9	1024	-737	0 6 4	* 26
0 2 10	1067	-953	0 6 -4	598 396
0 2 -10	1095	991	0 6 5	1591 1622
0 2 11	1605	1413	0 6 -5	429 -325
0 2 -11	1308	-1086	0 6 6	454 -304
0 2 12	482	343	0 6 -6	1141 1083
0 2 -12	*	239	0 6 7	1572 1580
0 2 13	*	-131	0 6 -7	1024 -998
0 2 -13	*	-56	0 6 8	708 -677
0 2 14	*	125	0 6 -8	713 623
0 2 -14	1026	-1051	0 6 9	* -223
0 2 15	872	-1056	0 6 -9	554 472
0 2 -15	474	339	0 6 10	1177 1143
0 2 16	*	144	0 6 -10	1161 -1123
0 2 -16	1054	-1226	0 6 11	894 -899
0 2 17	*	-216	0 6 -11	941 1042
0 2 -17	318	-52	0 6 12	488 496
0 2 18	*	-742	0 6 -12	458 -307
0 2 -18	281	524	0 6 13	* 154
0 3 0	1375	1212	0 6 -13	629 500
0 3 1	2998	-3075	0 6 14	* -303
0 3 -1	2402	-2131	0 6 -14	756 1004
0 3 2	907	-604	0 6 15	397 527
0 3 -2	2597	-2443	0 6 -15	430 -584
0 3 3	1348	-1218	0 6 -16	511 753
0 3 -3	2845	2807	0 7 0	801 -598
0 3 4	4465	-4743	0 7 1	2861 2878
0 3 -4	2981	-2995	0 7 -1	538 467
0 3 5	1177	-972	0 7 2	849 -772
0 3 -5	350	218	0 7 -2	1827 1821
0 3 6	1613	-1450	0 7 3	968 -927
0 3 -6	323	-394	0 7 -3	1103 -1140
0 3 7	1021	865	0 7 4	* -436
0 3 -7	2632	-2524	0 7 -4	1304 1213
0 3 8	1321	1298	0 7 5	883 -879
0 3 -8	1190	957	0 7 -5	716 -737
0 3 9	1428	-1367	0 7 6	933 802
0 3 -9	1745	-1630	0 7 -6	546 -389
0 3 10	2573	2727	0 7 7	592 -611
0 3 -10	450	101	0 7 -7	619 579
0 3 11	477	-256	0 7 8	482 226
0 3 -11	680	513	0 7 -8	1355 -1527
0 3 12	2549	-2599	0 7 9	1372 1396
0 3 -12	1207	-1257	0 7 -9	520 616
0 3 13	549	-463	0 7 10	491 -517
0 3 -13	939	962	0 7 -10	470 203
0 3 14	1096	-1283	0 7 11	* 173
0 3 -14	549	-488	0 7 -11	552 -560
0 3 15	470	452	0 7 12	* 99
0 3 -15	693	-804	0 7 -12	709 944
0 3 16	388	-389	0 7 13	501 -665
0 3 -16	400	317	0 7 -13	* -255
0 3 17	269	-362	0 7 14	708 1010
0 3 -17	498	-656	0 7 -14	* 131
0 4 0	1864	-1925	0 7 -15	273 342
0 4 1	1965	1982	0 8 0	* -294
0 4 -1	2369	2418	0 8 1	2902 -2953
0 8 -1	1454	1437	1 0 -15	1123 1181
0 8 2	1527	-1507	1 0 16	803 946
0 8 -2	495	391	1 0 -16	426 391
0 8 3	519	438	1 0 17	* -84
0 8 -3	*	10	1 0 -17	* -55
0 8 4	816	-928	1 0 -18	270 322
0 8 -4	480	321	1 1 0	231 -191
0 8 5	*	32	1 1 1	808 -795
0 8 -5	1159	1077	1 1 -1	497 516
0 8 6	621	686	1 1 2	1377 1313
0 8 -6	918	-924	1 1 -2	4005 -4840
0 8 7	*	220	1 1 3	2099 -2203
0 8 -7	1391	-1525	1 1 -3	2819 3557
0 8 8	496	500	1 1 4	745 547
0 8 -8	546	470	1 1 -4	1580 1590
0 8 9	565	-716	1 1 5	1761 1667
0 8 -9	824	-741	1 1 -5	571 508
0 8 10	*	-68	1 1 6	675 -609
0 8 -10	*	-11	1 1 -6	2313 2489
0 8 11	*	-147	1 1 7	1938 1914
0 8 -11	437	161	1 1 -7	1243 -1269
0 8 12	*	-243	1 1 8	597 273
0 8 -12	680	-743	1 1 -8	1644 1517
0 8 13	*	297	1 1 9	689 -607
0 8 -13	*	157	1 1 -9	814 -654
0 8 -14	*	-177	1 1 10	1879 1344
0 9 0	1183	-974	1 1 -10	2062 -1760
0 9 1	742	-660	1 1 11	1074 -960
0 9 -1	*	258	1 1 -11	1011 1112
0 9 2	621	585	1 1 12	561 413
0 9 -2	1796	-1963	1 1 -12	766 -615
0 9 3	1170	-1075	1 1 13	592 552
0 9 -3	824	863	1 1 -13	561 208
0 9 4	713	681	1 1 14	547 -502
0 9 -4	515	506	1 1 -14	621 704
0 9 5	*	-250	1 1 15	1265 1257
0 9 -5	885	-915	1 1 -15	803 -805
0 9 6	487	-424	1 1 16	532 -500
0 9 -6	977	920	1 1 -16	457 -68
0 9 7	610	620	1 1 17	* -97
0 9 -7	*	-237	1 1 -17	* -322
0 9 8	650	-761	1 1 -18	* 129
0 9 -8	*	-153	1 -1 0	4224 6675
0 9 9	*	82	1 -1 1	1328 1448
0 9 -9	408	-296	1 -1 -1	3203 4453
0 9 10	*	167	1 -1 2	3050 -3569
0 9 -10	798	-939	1 -1 -2	288 174
0 9 11	668	-809	1 -1 3	1785 1858
0 9 -11	520	651	1 -1 -3	2685 -2727
0 9 12	*	353	1 -1 4	1165 1086
0 9 -12	*	119	1 -1 -4	3142 3594
0 9 -13	*	-254	1 -1 5	2966 -2993
0 10 0	*	13	1 -1 -5	1344 1317
0 10 1	448	183	1 -1 6	997 -870
0 10 -1	833	-859	1 -1 -6	1222 -1096
0 10 2	748	-917	1 -1 7	2670 2439
0 10 -2	485	466	1 -1 -7	1351 1077
0 10 3	*	84	1 -1 8	522 450
0 10 -3	*	182	1 -1 -8	1329 -1260
0 10 4	*	165	1 -1 9	956 829
0 10 -4	*	358	1 -1 -9	1518 1284
0 10 5	*	-286	1 -1 10	488 -373
0 10 -5	*	117	1 -1 -10	470 -270
0 10 6	429	556	1 -1 11	813 -820
0 10 -6	713	-793	1 -1 -11	* 180
0 10 7	*	-80	1 -1 12	748 640
0 10 -7	655	787	1 -1 -12	1322 1057
0 10 8	*	349	1 -1 13	467 -5
0 10 -8	*	-381	1 -1 -13	* -135
0 10 9	*	306	1 -1 14	1119 1099
0 10 -9	*	-367	1 -1 -14	618 494
0 10 10	257	-394	1 -1 15	* -16
0 10 -10	419	527	1 -1 -15	509 -120
0 10 -11	*	-461	1 -1 16	* -95
0 11 0	509	577	1 -1 -16	* -177
0 11 1	456	-656	1 -1 17	740 924
0 11 -1	*	-8	1 -1 -17	445 629
0 11 2	548	536	1 -1 -18	* -378
0 11 -2	564	-424	1 2 0	3292 -3921
0 11 3	*	-33	1 2 1	779 811
0 11 -3	*	350	1 2 -1	844 -747
0 11 4	*	-195	1 2 2	3014 -3372
0 11 -4	*	-282	1 2 -2	2062 2171
0 11 5	766	1028	1 2 3	1051 -982
0 11 -5	*	360	1 2 -3	1670 -1730
0 11 6	294	353	1 2 4	893 722
0 11 -6	*	271	1 2 -4	759 885
0 11 7	308	445	1 2 5	2506 -2596
0 11 -7	470	-193	1 2 -5	276 88
0 11 -8	*	604	1 2 6	2461 2112
0 11 -9	*	-108	1 2 -6	945 -870
0 12 0	268	-295	1 2 7	602 -585
0 12 1	*	-100	1 2 -7	414 462
0 12 -1	323	358	1 2 8	633 -535
0 12 2	*	77	1 2 -8	2678 -2933
0 12 -2	382	238	1 2 9	1846 1682
0 12 3	*	260	1 2 -9	691 578
0 12 -3	*	400	1 2 10	753 -530
0 12 -4	*	295	1 2 -10	1061 1022
0 12 -5	*	-511	1 2 11	518 425
1 0 0	952	-1544	1 2 -11	1825 -1815
1 0 1	2600	3215	1 2 12	1589 -1357
1 0 -1	2116	-3400	1 2 -12	791 869
1 0 2	4053	-5589	1 2 13	1290 -1159
1 0 -2	6476	11324	1 2 -13	580 -525
1 0 3	1344	1375	1 2 14	771 724
1 0 -3	4869	6078	1 2 -14	458 424
1 0 4	1430	-1529	1 2 15	851 -804
1 0 -4	1763	1789	1 2 -15	* 363
1 0 5	2256	2148	1 2 16	* -268
1 0 -5	624	750	1 2 -16	825 -1044
1 0 6	3140	3378	1 2 17	398 565
1 0 -6	893	-711	1 2 -17	* 477
1 0 7	1337	-1120	1 2 -18	343 -612
1 0 -7	1274	1079	1 -2 0	3404 3885
1 0 8	2881	2642	1 -2 1	4562 -6539
1 0 -8	2115	-1781	1 -2 -1	552 -423
1 0 9	*	-179	1 -2 2	1291 1393
1 0 -9	1479	-1288	1 -2 -2	1417 -1348
1 0 10	557	-369	1 -2 3	359 -310
1 0 -10	2276	2032	1 -2 -3	2630 2632
1 0 11	2018	2023	1 -2 4	2263 -2366
1 0 -11	*	-273	1 -2 -4	2169 -2227
1 0 12	662	-875	1 -2 5	2056 2255
1 0 -12	628	650	1 -2 -5	1004 916
1 0 13	554	316	1 -2 6	2018 -1840
1 0 -13	849	925	1 -2 -6	1057 -894
1 0 14	526	360	1 -2 7	760 731
1 0 -14	1154	-1223	1 -2 -7	2061 -2047
1 0 15	644	-622	1 -2 8	442 -133

Table 1 (*cont.*)

1	-2	-8	1197	897
1	-2	9	1961	-1739
1	-2	-9	1475	-1334
1	-2	10	1562	1379
1	-2		•	-73
1	-2	-10	•	1311
1	-2	11	1319	-992
1	-2	-11	1181	1006
1	-2	12	1153	-1030
1	-2	-12	1659	-1622
1	-2	13	550	95
1	-2	-13	914	849
1	-2	14	1308	-1311
1	-2	-14	1071	993
1	-2	15	725	737
1	-2	-15	458	-317
1	-2	16	408	341
1	-2	-16	448	552
1	-2	17	470	-628
1	-2	-17	524	-800
1	-2	-18	•	392
1	3	0	260	125
1	3	1	2763	-2988
1	3	-1	2631	-2853
1	3	2	3315	-3612
1	3	-2	1354	1272
1	3	3	577	-430
1	3	-3	1819	-1672
1	3	4	938	630
1	3	-4	2754	-3122
1	3	5	1342	1206
1	3	-5	1938	2015
1	3	6	•	-107
1	3	-6	828	-829
1	3	7	•	136
1	3	-7	467	-493
1	3	8	2142	1977
1	3	-8	•	-314
1	3	9	2192	-2176
1	3	-9	531	-499
1	3	10	3321	-3189
1	3	-10	665	463
1	3	11	•	61
1	3	-11	1450	-1317
1	3	12	707	-747
1	3	-12	519	-284
1	3	13	•	120
1	3	-13	663	695
1	3	14	•	-160
1	3	-14	665	-680
1	3	15	•	9
1	3	-15	•	-42
1	3	16	835	906
1	3	-16	•	341
1	3	-17	360	-488
1	-3	0	1315	-1344
1	-3	1	1296	1212
1	-3	-1	2090	-2282
1	-3	2	1317	-1208
1	-3	-2	1622	1647
1	-3	3	449	-413
1	-3	-3	1840	-1885
1	-3	4	1818	-1926
1	-3	-4	518	-473
1	-3	5	2124	-2127
1	-3	-5	•	61
1	-3	6	1910	1672
1	-3	-6	3462	-3412
1	-3	7	2121	-1876
1	-3	-7	772	-529
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2	3	0	1013	-938
2	3	1	920	846
2	3	-1	1963	-2182
2	3	2	464	262
2	3	-2	367	107
2	3	3	1435	1242
2	3	-3	1642	-1782
2	3	4	922	-769
2	3	-4	467	218
2	3	5	1379	1149
2	3	-5	418	439
2	3	6	•	-110
2	3	-6	2242	-2194
2	3	7	3303	-3245
2	3	-7	555	-463
2	3	8	1335	-1234
2	3	-8	889	794
2	3	9	1158	-188
2	3	-9	•	-294
2	3	10	•	-188
2	3	-10	•	-339
2	3	11	546	273
2	3	-11	630	-165
2	3	12	•	1
2	3	-12	717	535
2	3	13	•	273
2	3	-13	•	222
2	3	14	•	89
2	3	-14	1176	-1185
2	3	15	•	-692
2	3	-15	504	466
2	3	-16	394	43
2	3	-17	•	-440
2	-3	0	1013	-961
2	-3	1	1151	-1157
2	-3	-1	760	711
2	-3	2	1490	-1710
2	-3	-2	697	565
2	-3	3	750	955
2	-3	-3	2245	-2494
2	-3	4	•	-237
2	-3	-4	1027	1116
2	-3	5	1522	-1689
2	-3	-5	486	-430
2	-3	6	976	845
2	-3	-6	760	-809
2	-3	7	643	297
2	-3	-7	1022	851
2	-3	8	1428	-1356
2	-3	-8	1771	-1605
2	-3	9	•	-73
2	-3	-9	787	-558
2	-3	10	1126	-900
2	-3	-10	793	-767
2	-3	11	•	-264
2	-3	-11	655	-388
2	-3	12	•	-158
2	-3	-12	•	176
2	-3	13	908	-904
2	-3	-13	656	-517
2	-3	14	645	620
2	-3	-14	1058	939
2	-3	15	415	-386
2	-3	-15	783	1095
2	-3	-16	•	-510
2	4	0	1833	1643
2	4	1	•	-333
2	4	-1	1119	938
2	4	2	1019	975
2	4	-2	2175	-2062
2	4	3	732	-568
2	4	-3	1090	1107
2	4	4	796	-567
2	4	-4	897	-769
2	4	5	608	427
2	4	-5	•	-154
2	4	6	2240	-2021
2	4	-6	2147	1821
2	4	7	648	364
2	4	-7	1070	-838
2	4	8	681	669
2	4	-8	630	481
2	4	9	762	-677
2	4	-9	1291	-1171
2	4	10	892	876
2	4	-10	681	-556
2	4	11	740	-928
2	4	-11	765	884
2	4	12	535	222
2	4	-12	1526	-1537
2	4	13	505	560
2	4	-13	736	617
2	4	14	656	-792
2	4	-14	1103	1168
2	4	-15	•	-95
2	4	-16	360	250
2	-4	0	•	-111
2	-4	1	944	-930
2	-4	-1	1218	-1395
2	-4	2	1629	1642
2	-4	-2	1539	-1886
2	-4	3	889	-985
2	-4	-3	971	1048
2	-4	4	668	642
2	-4	-4	490	-643
2	-4	5	1748	1604
2	-4	-5	•	-211
2	-4	6	1944	-1833
2	-4	-6	636	456
2	-4	7	•	-255
2	-4	-7	2151	-1839
2	-4	8	838	-691
2	-4	-8	901	-715
2	-4	9	•	-181
2	-4	-9	691	514
2	-4	10	738	526
2	-4	-10	575	-104
2	-4	11	1066	-1120
2	-4	-11	824	780
2	-4	12	•	114
2	-4	-12	601	-180
2	-4	13	•	231
2	-4	-13	659	525
2	-4	14	587	-505
2	-4	-14	538	470
2	-4	15	437	515
2	-4	-15	1163	-1434
2	-4	-16	332	57
2	5	0	2120	-1882
2	5	1	1715	1519
2	5	-1	1578	1404
2	5	2	984	652
2	5	-2	889	681
2	5	3	833	-228
2	5	-3	•	-754
2	5	4	1396	1108
2	5	-4	1377	1037
2	5	5	1278	-1192
2	5	-5	717	-560
2	5	6	982	943
2	5	-6	601	485
2	5	7	•	-237
2	5	-7	1371	1083
2	5	8	923	-876
2	5	-8	•	-235
2	5	9	997	1136
2	5	-9	1045	1030
2	5	10	593	-381
2	5	-10	•	-242
2	5	11	563	346
2	5	-11	•	-481
2	5	12	615	610
2	5	-12	781	776
2	5	13	•	-234
2	5	-13	1302	-1374
2	5	14	464	245
2	5	-15	578	682
2	5	-16	•	81
2	6	0	541	250
2	6	1	1071	-1154
2	6	-1	1366	-1429
2	6	2	1476	-1146
2	6	-2	1508	1471
2	6	3	1704	1543
2	6	-3	•	248
2	6	4	1207	-1146
2	6	-4	•	-202
2	6	5	925	760
2	6	-5	1027	1116
2	6	6	3088	3412
2	6	-6	1806	-1512
2	6	7	•	30
2	6	-7	2102	1843
2	6	8	•	266
2	6	-8	767	600
2	6	9	928	-898
2	6	-9	1411	-1258
2	6	10	691	-539
2	6	-10	1269	1188
2	6	11	702	781
2	6	-11	684	-546
2	6	12	1449	-1394
2	6	-12	•	186
2	6	13	697	660
2	6	-13	•	-44
2	6	14	599	621
2	6	-14	515	-522
2	6	-15	537	701
2	6	0	1072	961
2	6	1	1302	-1214
2	6	-1	•	164
2	6	2	1171	909
2	6	-2	739	717
2	6	3	803	707
2	6	-3	655	507
2	6	4	1530	-1371
2	6	-4	1139	-1035
2	6	5	681	576
2	6	-5	1704	1616
2	6	6	723	622
2	6	-6	•	-402
2	6	7	•	-79
2	6	-7	•	-142
2	6	8	•	482
2	6	-8	962	1111
2	6	9	•	-248
2	6	-9	758	-689
2	6	10	601	445
2	6	-10	694	709
2	6	11	728	790
2	6	-11	•	-85
2	6	12	•	120
2	6	-12	568	-525
2	6	13	•	750
2	6	-13	634	728
2	6	-14	389	-237
2	6	-15	•	-152
2	-6	0	•	-164
2	-6	1	•	78
2	-6	-1	1838	1540
2	-6	2	•	117
2	-6	-2	912	-793
2	-6	3	896	-711
2	-6	-3	799	670
2	-6	4	1051	1121
2	-6	-4	1653	1445
2	-6	5	•	-159
2	-6	-5	•	-258
2	-6	6	•	-209
2	-6	-6	•	-17
2	-6	7	891	638
2	-6	-7	689	157
2	-6	8	787	806
2	-6	-8	845	770
2	-6	9	1410	1481
2	-6	-9	•	-63
2	-6	10	•	-60
2	-6	-10	•	-324
2	-6	11	643	-592
2	-6	-11	800	719
2	-6	12	850	945
2	-6	-12	584	548
2	-6	13	476	-221
2	-6	-13	538	-623
2	-6	14	•	-561
2	-6	-14	•	97
2	7	0	1028	836
2	7	1	927	-1001
2	7	-1	679	-415
2	7	2	655	629
2	7	-2	2432	-2603
2	7	3	•	-13
2	7	-3	769	618
2	7	4	918	942
2	7	-4	1045	951
2	7	5	•	315
2	7	-5	630	-244
2	7	6	1124	-1255
2	7	-6	•	324
2	7	7	701	717
2	7	-7	•	83
2	7	8	•	-508
2	7	-8	741	615
2	7	9	•	127
2	7	-9	•	73
2	7	10	789	999
2	7	-10	674	-729
2	7	11	415	-515
2	7	-11	509	570
2	7	-12	488	-441
2	7	-13	392	-246
2	7	-14	•	437
2	-7	0	•	-78
2	-7	1	1364	-1172
2	-7	-1	859	663
2	-7	2	930	830
2	-7	-2	•	-114
2	-7	3	•	-88
2	-7	-3	•	262
2	-7	4	869	-705
2	-7	-4	1015	-777
2	-7	5	1471	1241
2	-7	-5	1714	1533
2	-7	6	738	-524
2	-7	-6	1903	1702
2	-7	7	•	393
2	-7	-7	1451	-1389
2	-7	8	915	774
2	-7	-8	767	750
2	-7	9	932	-784
2	-7	-9	•	89
2	-7	10	585	508
2	-7	-10	591	-510
2	-7	11	576	-436
2	-7	-11	•	-137
2	-7	12	•	117
2	-7	-12	672	-698
2	-7	13	374	501
2	-7	-13	620	851
2	8	0	•	134
2	8	1	902	1036
2	8	-1	•	-250
2	8	2	743	-769
2	8	-2	756	776
2	8	3	•	484
2	8	-3	1919	-1926
2	8	4	•	-292
2	8	-4	787	-650
2	8	5	758	-829
2	8	-5	601	-476
2	8	6	531	308
2	8	-6	615	-437
2	8	7	•	-460
2	8	-7	773	940
2	8	8	•	29
2	8	-8	568	-537
2	8	9	•	282
2	8	-9	575	608
2	8	10	•	-662
2	8	-10	526	549
2	8	-11	619	-795
2	8	-12	•	322
2	-8	0	689	-239
2	-8	1	•	164
2	-8	-1	•	-382
2	-8	2	1718	-1607
2	-8	-2	1175	1132
2	-8	3	•	183
2	-8	-3	•	139
2	-8	4	•	-293
2	-8	-4	1653	1517
2	-8	5	663	-373
2	-8	-5	•	-62
2	-8	6	694	638
2	-8	-6	1619	-1422
2	-8	7	665	-659
2	-8	-7	•	-123
2	-8	8	•	-219
2	-8	-8	614	-852
2	-8	9	•	274
2	-8	-9	•	-129
2	-8	10	•	-89
2	-8	-10	•	120
2	-8	11	617	528
2	-8	-11	•	-101
2	-8	-12	367	404

Table 1 (*cont.*)

Table 2(*a*). *The final coordinates with their e.s.d. (in parenthesis)*

	X/a	*Y/b*	*Z/c*
Cl(1)	0·8474 (6)	0·3725 (3)	0·3831 (1)
C(1)	0·5640 (22)	0·5320 (9)	0·2387 (6)
C(2)	0·6274 (22)	0·3965 (9)	0·2733 (6)
C(3)	0·5087 (24)	0·2756 (10)	0·2180 (6)
C(4)	0·3422 (24)	0·2857 (9)	0·1288 (6)
C(5)	0·2931 (26)	0·4191 (10)	0·0925 (6)
C(6)	0·4017 (25)	0·5392 (10)	0·1477 (6)
C(7)	0·6663 (23)	0·6656 (9)	0·2934 (5)
C(8)	0·8147 (26)	0·7779 (10)	0·2489 (6)
C(9)	0·8867 (27)	0·9074 (10)	0·2450 (7)
C(10)	0·8012 (27)	0·9247 (12)	0·3872 (7)
C(11)	0·6510 (26)	0·8167 (10)	0·4327 (6)
C(12)	0·5845 (25)	0·6842 (10)	0·3872 (6)
C(13)	0·2731 (24)	0·1599 (10)	0·0702 (6)
O(1)	0·2876 (23)	0·0383 (8)	0·1051 (5)
O(2)	0·0233 (21)	0·1733 (8)	−0·0024 (5)

Table 2(*b*). *Orthogonal coordinates for the heavy atoms*

Coordinates with respect to the axes:

$X' = X \sin\gamma + Z(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma$
$Y' = Y + X\cos\gamma + Z\cos\alpha$
$Z' = Z[\sin^2\alpha - \{(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma\}^2]^{1/2}$

	X'	*Y'*	*Z'*
Cl(1)	2·723 Å	3·226 Å	5·400 Å
C(1)	1·837	4·868	3·364
C(2)	2·031	3·546	3·853
C(3)	1·653	2·439	3·073
C(4)	1·139	2·607	1·815
C(5)	1·002	3·907	1·304
C(6)	1·342	5·008	2·081
C(7)	2·153	6·099	4·135
C(8)	2·797	7·169	3·508
C(9)	3·008	8·371	4·158
C(10)	2·537	8·504	5·457
C(11)	1·884	7·476	6·100
C(12)	1·693	6·243	5·457
C(13)	0·702	1·458	0·989
O(1)	0·962	0·266	1·481
O(2)	0·094	1·652	−0·034

plied to positional, thermal and scale factors the hydrogen atoms were fixed at distances of 1·08 Å for those attached to the phenyl rings and at 0·97 Å for that bonded to O(1).

The weighting scheme

$$w = 1/(2|F_{\min}| + |F_o| + 2/|F_{\max}| \cdot |F_o|^2 + 5/|F_{\max}|^2 \cdot |F|^3)$$

was employed. Refinement converged at a residual of $R = 0{\cdot}135$; the weighting scheme analysis was satisfactory after omitting the $10\bar{2}$ reflexion. This reflexion together with the 102, $10\bar{3}$, $11\bar{1}$, $1\bar{1}\bar{1}$ and $1\bar{2}1$ were suspected of suffering from extinction, and by individually scaling F_o to F_c for these reflexions the residual was reduced to 0·127.

A final three-dimensional electron density distribution and a difference electron density distribution were calculated. The latter synthesis indicated no discrepancies in the structure, having only a few positions with a maximum value of about 0·5 e.Å^{-3} which did not correspond to atom sites.

The final structure factors are given in Table 1; those reflexions which were not observed in the regions of reciprocal space examined, either because of camera geometry or from being too weak to measure, are marked with an asterisk. Table 2 gives the heavy atom coordinates and Table 3 their thermal parameters. The idealized hydrogen parameters appear in Table 4.

Table 4. *Idealized hydrogen atom coordinates*

H(1) is attached to O(1) and the numbers of the remaining hydrogen atoms correspond to that of the carbon atom to which they are attached.

	X/a	*Y/b*	*Z/c*
H(1)	0·171	0·960	0·067
H(3)	0·553	0·174	0·245
H(5)	0·165	0·428	0·021
H(6)	0·358	0·640	0·120
H(8)	0·875	0·763	0·179
H(9)	0·011	0·998	0·258
H(10)	0·849	0·023	0·422
H(11)	0·589	0·835	0·505
H(12)	0·467	0·594	0·425

Table 3. *Thermal parameters in* Å^2 *for the heavy atoms with their e.s.d. (in parenthesis)*

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl(1)	0·028 (1)	0·037 (1)	0·023 (1)	−0·005 (2)	0·008 (2)	−0·003 (2)
C(1)	0·011 (5)	0·032 (5)	0·030 (4)	0·020 (7)	0·011 (6)	−0·009 (6)
C(2)	0·010 (5)	0·026 (4)	0·032 (4)	0·016 (7)	0·006 (6)	0·026 (6)
C(3)	0·022 (6)	0·037 (5)	0·031 (4)	0·007 (8)	0·014 (7)	−0·010 (7)
C(4)	0·025 (6)	0·025 (4)	0·030 (4)	−0·002 (7)	−0·010 (6)	0·004 (7)
C(5)	0·040 (6)	0·028 (4)	0·025 (4)	0·016 (8)	−0·008 (6)	0·004 (7)
C(6)	0·030 (6)	0·034 (5)	0·028 (4)	0·013 (8)	0·003 (7)	−0·018 (7)
C(7)	0·020 (5)	0·029 (4)	0·021 (3)	0·004 (7)	0·005 (6)	0·028 (6)
C(8)	0·034 (6)	0·026 (4)	0·034 (4)	0·012 (8)	0·009 (7)	0·025 (8)
C(9)	0·035 (7)	0·024 (5)	0·055 (6)	0·003 (8)	0·007 (8)	0·001 (9)
C(10)	0·034 (7)	0·040 (5)	0·044 (5)	0·008 (9)	0·004 (8)	−0·009 (9)
C(11)	0·031 (6)	0·036 (5)	0·036 (4)	0·010 (9)	−0·015 (7)	0·012 (8)
C(12)	0·032 (6)	0·037 (5)	0·027 (4)	0·014 (8)	−0·005 (7)	0·002 (7)
C(13)	0·020 (6)	0·034 (5)	0·039 (4)	0·007 (8)	−0·010 (7)	0·015 (7)
O(1)	0·081 (6)	0·028 (4)	0·043 (4)	0·001 (8)	0·004 (6)	−0·011 (7)
O(2)	0·061 (5)	0·042 (4)	0·035 (3)	0·012 (8)	−0·001 (6)	−0·027 (7)

The arrangement of the molecules in the unit cell as viewed along the *a* axis is shown in Fig. 3; the bond lengths and bond angles together with some of the intramolecular non-bonded distances are in Table 7. The equations of the mean planes of the ring systems C(1)–C(6); C(1)–C(6) and chlorine; C(7)–C(12) and the group C(4), C(13), O(1) and O(2) calculated with respect to the orthogonal triad a',b',c', where b' coincides with b, a' is the projection of a on the plane perpendicular to b', and c' is perpendicular to a' and b', are:

$$0{\cdot}9269X'-0{\cdot}0277Y'-0{\cdot}3742Z'=0{\cdot}3239$$
$$0{\cdot}9185X'-0{\cdot}0241Y'-0{\cdot}3948Z'=0{\cdot}2778$$
$$0{\cdot}8783X'-0{\cdot}3277Y'+0{\cdot}3481Z'=1{\cdot}3379$$
$$0{\cdot}8689X'+0{\cdot}0009Y'-0{\cdot}4949Z'=0{\cdot}1076\,.$$

The deviations of the atoms from the mean planes are quoted in Table 5. All intermolecular contacts less than 4 Å were calculated and the shortest are quoted in Table 6. The angle between the carboxylic group and the phenyl ring C(1)–C(6) is 7·9° and the angle between the two phenyl rings is 46·1°.

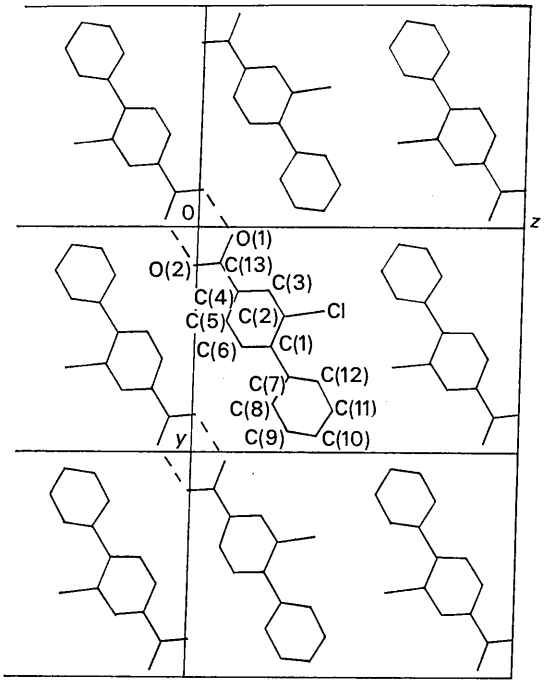

Fig. 3. The arrangement of the molecules in the unit cell viewed along the *a* axis.

Table 6. *Intermolecular distances between atoms less than* 3·6 Å *apart (excluding hydrogen atoms)*

i	*j*	Equipoint indication	d_{ij}
C(13)	O(1)	$\bar{x}$, $\bar{y}$, $\bar{z}$	3·440 Å
C(13)	O(2)	$\bar{x}$, $\bar{y}$, $\bar{z}$	3·349
O(1)	O(1)	$\bar{x}$, $\bar{y}$, $\bar{z}$	3·571
O(1)	O(2)	$\bar{x}$, $\bar{y}$, $\bar{z}$	2·624
O(2)	O(2)	$\bar{x}$, $\bar{y}$, $\bar{z}$	3·310
C(2)	Cl	$x+1$, y, z	3·559
C(4)	O(2)	$x+1$, y, z	3·576
C(7)	C(8)	$x+1$, y, z	3·531
C(11)	C(9)	$x+1$, y, z	3·544
C(11)	C(10)	$x+1$, y, z	3·512
C(12)	C(8)	$x+1$, y, z	3·573
C(13)	O(2)	$x+1$, y, z	3·441
O(1)	O(2)	$x+1$, y, z	3·597
C(5)	C(5)	$\bar{x}+1$, $\bar{y}+1$, z	3·581

Discussion

The angle of 7·9° between the phenyl ring and the carboxyl group is similar to a value of 5·6° obtained for 2′-chlorobiphenyl-4-carboxylic acid (Sutherland, 1969) and somewhat larger than the value of 3·3° determined in *p*-nitrobenzoic acid (Sakore & Pant, 1966). A similar value of 7·9° has been determined between the plane of the phenyl ring and the acetyl radical in 4-acetyl-2′-chlorobiphenyl (Sutherland & Hoy, 1968).

Table 5. *Deviations of the atoms* (Å) *from the planes*

(I)	$0{\cdot}9269X'-0{\cdot}0277Y'-0{\cdot}3742Z'=0{\cdot}3239$	C(1)–C(6)
(II)	$0{\cdot}9185X'-0{\cdot}0241Y'-0{\cdot}3948Z'=0{\cdot}2778$	C(1)–C(6) and Cl
(III)	$0{\cdot}8783X'-0{\cdot}3277Y'+0{\cdot}3481Z'=1{\cdot}3379$	C(7)–C(12)
(IV)	$0{\cdot}8689X'+0{\cdot}0009Y'-0{\cdot}4949Z'=0{\cdot}1076$	C(4), C(13), O(1) and O(2)

	(I)	(II)	(III)	(IV)
Cl	+0·090 Å	−0·014 Å		
O(1)	+0·005	+0·014		+0·001 Å
O(2)	−0·269	−0·218		+0·001
C(1)	+0·008	+0·029	−0·149 Å	−0·172
C(2)	−0·008	+0·030		
C(3)	+0·001	+0·023		
C(4)	+0·006	−0·002	−0·560	+0·001
C(5)	−0·007	−0·031		
C(6)	−0·001	−0·010		
C(7)	−0·045	−0·080	+0·001	−0·278
C(8)			+0·005	
C(9)			+0·006	
C(10)	−0·250	−0·307	+0·002	−0·597
C(11)			+0·003	
C(12)			−0·005	
C(13)	−0·074	−0·059	−0·855	−0·005

Values similar to 46·1°, for the angle between the two phenyl rings, have been obtained for 2′-chlorobiphenyl-4-carboxylic acid (48·9°) and 4-acetyl-2′-chlorobiphenyl (49·2°).

The C–Cl bond length of 1·725 Å is considerably larger than the value published in volume III of *International Tables for X-ray Crystallography* (1962) of 1·70 ± 0·01 Å. In *o*-chlorobenzoic acid (Ferguson & Sim, 1961), the C–Cl distance was determined as 1·737 Å, and in 4-acetyl-2′-chlorobiphenyl as 1·738 Å, which are similar to the value in the present analysis.

Both the C(1)–C(7) bond of 1·487 Å and the C(4)–C(13) bond of 1·482 Å do not differ significantly from the theoretical value of 1·477 quoted by Dewar & Schmeising (1959) and Cruickshank & Sparks (1960) for the sp^2 single bond between trigonally linked carbon atoms.

The C(1)–C(7) bond length of 1·487 ± 0·012 Å is similar to those of 1·479 ± 0·010 Å in 4-acetyl-2′-fluorobiphenyl (Young, Tollin & Sutherland, 1968), 1·490 ± 0·010 Å in 4-acetyl-2′-chlorobiphenyl, and is not significantly different from the biphenyl bond of 1·502 ± 0·010 Å in 2′-chlorobiphenyl-4-carboxylic acid.

The exocylic bond C(4)–C(13) of 1·482 ± 0·013 Å compares favourably with the value of 1·477 ± 0·011 Å in 2′-chlorobiphenyl-4-carboxylic acid.

The displacement of the chlorine atom from the phenyl ring C(1)–C(6) of +0·090 Å corresponds to the C(2)–Cl bond bending out of the plane of the ring through an angle of 3°. A similar bending of 1·8° for the C–Cl bond was obtained in 2′-chlorobiphenyl-4-carboxylic acid. Displacements of −0·045 Å and −0·074 Å were obtained for C(7) and C(13) from the ring C(1)–C(6).

It would appear that, whereas biphenyl in the solid phase is planar, the introduction of the chlorine atom in the 2 position causes a strain which results in the twisting of the two phenyl rings about the phenyl bond, the displacement of the ring C(7)–C(12) along the line C(10), C(7), C(1) and C(6), and the displacement of the chlorine out of the plane of the phenyl ring C(1)–C(6). The carboxyl group is displaced from the plane of the ring C(1)–C(6), Table 5, and rotated about the C(4)–C(13) bond. These results can be explained in terms of a relayed steric effect similar to that observed by Ferguson & Sim (1962) in 2-chloro-5-nitrobenzoic acid.

The C(13)–O(1) bond of 1·315 ± 0·012 Å and C(13)–O(2) bond of 1·205 ± 0·012 Å is similar to those obtained for *o*-chlorobenzoic acid (Ferguson & Sim, 1961). The O–H···O bond of 2·62 Å, which is the shortest intermolecular distance, is similar to that of 2·61 Å obtained in 2′-chloro-4-carboxylic acid.

Table 7. *Bond lengths and bond angles*

The bond lengths are in Å ±0·01 Å and the angles are in degrees ±1·0°.

	Length		Length
Cl(1)–C(2)	1·725 Å	C(2)—C(3)	1·406 Å
Cl(1)–C(7)	3·191	C(3)—C(4)	1·369
Cl(1)–C(12)	3·189	C(4)—C(5)	1·404
O(1) –C(3)	2·781	C(4)—C(13)	1·482
O(1) –C(4)	2·372	C(5)—C(6)	1·389
O(1) –C(13)	1·315	C(7)—C(8)	1·398
O(2) –C(4)	2·328	C(7)—C(12)	1·406
O(2) –C(5)	2·775	C(8)—C(9)	1·382
O(2) –C(13)	1·205	C(9)—C(10)	1·389
C(1) –C(2)	1·423	C(10)–C(11)	1·377
C(1) –C(6)	1·382	C(11)–C(12)	1·403
C(1) –C(7)	1·487		

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Table 7 (*cont.*)

	Angle		Angle
Cl(1) –C(2)—C(1)	122·4°	C(2)—C(1)—C(7)	124·2°
Cl(1) –C(2)—C(3)	117·3	C(6)—C(1)—C(7)	118·3
O(1)—C(13)–C(4)	115·9	C(1)—C(7)—C(12)	120·2
O(1)—C(13)–O(2)	124·3	C(1)—C(7)—C(8)	120·0
O(2)—C(13)–C(4)	119·8	C(7)—C(8)—C(9)	121·7
C(13)–C(4)—C(5)	119·1	C(8)—C(9)—C(10)	118·2
C(13)–C(4)—C(3)	121·9	C(9)—C(10)–C(11)	121·7
C(1)—C(2)—C(3)	120·3	C(10)–C(11)–C(12)	120·3
C(2)—C(3)—C(4)	120·9	C(11)–C(12)–C(7)	118·4
C(3)—C(4)—C(5)	119·0	C(12)–C(7)—C(8)	119·6
C(4)—C(5)—C(6)	120·4		
C(5)—C(6)—C(1)	117·5		

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Kristall- und Molekülstruktur von 4,5-Dioxo-2-thioxo-1,3-dithiolan (β-Modifikation)*

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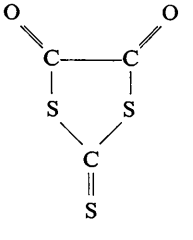
The crystal structure of the β form of 4,5-dioxo-2-thioxo-1,3-dithiolane, $C_3O_2S_3$, has been determined ($a=16{\cdot}758$, $b=5{\cdot}688$, $c=6{\cdot}313$ Å, $\beta=107{\cdot}1°$, space group $P2_1/a$, $Z=4$) by the symbolic addition method. The least-squares refinement converged to an R index of 6·7%. The molecule, including the CS_3 group, is almost planar. The bond distances indicate a certain amount of π electron delocalization, although the exocyclic C–O (1·195 Å) and C–S (1·608 Å) bond distances are very close to the values generally accepted as double bond distances. The results of the structure determination are in accordance with the bonding data from a Hückel molecular orbital calculation. The structure shows an unusually short intermolecular C(sp^2)···O(carbonyl) contact of 2·90 Å. This is a new example of a specific structure determining intermolecular interaction between the charge centres of $C^{\delta+}$–$O^{\delta-}$ dipoles in polycarbonyl compounds.

4,5-Dioxo-2-thioxo-1,3-dithiolan (I) entsteht in Form tiefroter Kristalle bei der Reaktion von Trithiokohlensäure mit Oxalylchlorid (Krebs & Gattow, 1963). Im Rahmen unserer Untersuchungen an Verbindungen mit einer CS_3-Gruppe und besonders für die detaillierte Diskussion der Bindungs- und Mesomerieverhältnisse



(I)

in der vorliegenden interessanten Ringverbindung (vgl. Müller, Krebs & Ahlrichs, 1966) erschien die Kenntnis der exakten Struktur des $C_3O_2S_3$ wichtig. Ausser der Kristallstruktur der Trithiokohlensäure bei -100 °C (Krebs & Gattow, 1965) und derjenigen des $[(C_6H_5)_4As]_2Ni(CS_3)_2$ (McKechnie, Miesel & Paul, 1967) sind bisher keine weiteren Strukturen von Verbindungen bekannt, die eine CS_3-Gruppe enthalten.

Nadelförmige Kristalle der α-Modifikation (Krebs & Gattow, 1963) entstehen, wenn die konzentrierte Lösung der Substanz in Petroläther auf Temperaturen unterhalb etwa 0 °C abgekühlt wird. Die hier untersuchte β-Modifikation bildet sich dagegen, wenn die Lösung von $C_3O_2S_3$ in Petroläther oberhalb etwa 30° unter Ausschluss von Feuchtigkeit langsam eindunstet. Die thermodynamischen Stabilitätsverhältnisse der beiden Modifikationen sind noch nicht geklärt.

Experimentelles

Die aus Petroläther bei *ca.* 35 °C gewonnenen und einige Male umkristallisierten Kristalle bilden kompakte monokline Prismen. Gitterkonstanten und Raumgruppe wurden aus Precession-Aufnahmen bestimmt; die genauen Abmessungen der Elementarzelle bei Zimmertemperatur wurden mit Hilfe des Einkristalldiffraktometers verfeinert. Die systematischen Auslöschungen ($h0l$ nur mit $h=2n$ und $0k0$ nur mit $k=2n$ vorhanden) ergaben die Raumgruppe $P2_1/a$ (C_{2h}^5). Die ermittelten

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