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The Crystal Structure of 4-Acetyl-2′-Chlorobiphenyl

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The crystal structure of 4-acetyl-2′-chlorobiphenyl ($C_{14}H_{11}OCl$) has been determined from three-dimensional X-ray diffraction data by a Patterson searching method. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=4{\cdot}00$, $b=38{\cdot}51$, $c=7{\cdot}52$ Å, $\beta=100{\cdot}07°$. The structure was refined with use of anisotropic thermal parameters to a residual of 11% for the 883 observed structure factors. The angle between the two phenyl rings was found to be 49·2°. All the intermolecular contacts correspond to normal van der Waals interactions.

Introduction

This paper describes an X-ray crystallographic study of 4-acetyl-2′-chlorobiphenyl, the second in the series of substituted biphenyl derivatives under investigation, the first being 4-acetyl-2′-fluorobiphenyl (Young, Tollin & Sutherland, 1968).

The structure was also of interest as it provided an opportunity of applying the $I(\theta,\varphi)$ method of Tollin & Cochran (1964) to an analysis where a heavy atom and a short axis were present. The heavy atom could not on its own determine sufficient phases to solve the structure.

Experimental

The space group and unit-cell dimensions were obtained from precession and Weissenberg photographs using Cu $K\alpha$ and Mo $K\alpha$ radiations; the systematic absences $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$ uniquely determined the space group as $P2_1/c$, the unit-cell dimensions being $a=4{\cdot}00\pm0{\cdot}01$, $b=38{\cdot}51\pm0{\cdot}01$, $c=7{\cdot}52\pm0{\cdot}01$ Å, $\beta=100{\cdot}07\pm0{\cdot}08°$.

The density measured at 17°C by the method of flotation using aqueous cadmium n-dodecatungstaborate was determined to be 1·36 g.cm^{-3}. The calculated value, assuming four molecules per unit cell, was 1·34 g.cm^{-3}.

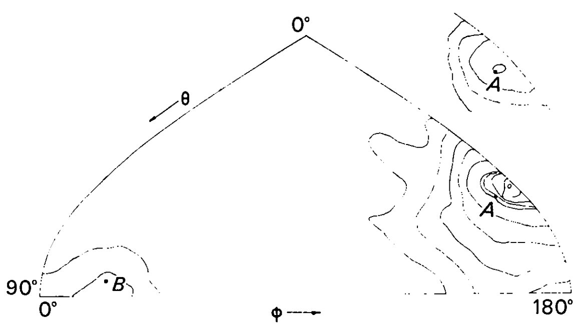

Fig. 1. The $I(\theta,\varphi)$ function for the 78 largest $°F_s$ terms. Insert shows details of the largest peak with full 3-D data. A and B indicate final positions of the normals.

The crystals were semi-transparent needles with poorly defined faces. Some gave rise to faint intermediate layer lines of 12 Å spacing when rotated about the a axis, suggesting that a superlattice was present. Several crystals of approximately the same dimensions were examined and one which did not appear to exhibit the 12 Å spacing was chosen for intensity data collection. This crystal had dimensions of 0·003 × 0·002 cm perpendicular to the needle axis.

Diffraction data for the $0kl$ to $3kl$ and $hk0$ zones were collected by the multiple-film equi-inclination method using Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a calibrated scale. Corrections were applied for Lorentz and polarization factors, and, for the non-zero levels, the Phillips (1954) correction factor and the data reduced to an arbitrary scale using programs written by the authors. No correction was applied for absorption.

Structure determination

The coordinates of the chlorine atom at −0·74, 7·84, 0·14 Å were obtained from the Harker peaks of an unsharpened three-dimensional Patterson synthesis.

To obtain the orientation of the rings the method of Tollin & Cochran (1964) was employed. An 'origin peak removed' $I(\theta,\varphi)$ function was computed from the 78 largest $°|F_s(h)|^2$ terms and $R=3{\cdot}5$ Å, $°|F_s(h)|^2$ being defined as

$$(F_o^2-\Sigma f_Q^2)\exp(B\sin^2\theta/\lambda^2)/\sum_Q f_Q^2\,,$$

where B had a value of 3. This showed one large peak in the region of $\theta=56°$, $\varphi=168°$ where θ,φ are the spherical polar angles referred to the orthogonal triad $\mathbf{a}^*\mathbf{b}^*\mathbf{c}$, Fig. 1. The coordinates of the maxima, which corresponds to the benzene ring attached to the chlorine, were obtained from an $I(\theta,\varphi)$ function computed in the region of this peak using all the $°|F_s(h)|^2$ data. There was no clearly defined second peak which corresponded to the other benzene ring plus acetyl group.

The section through the Patterson function, computed in the orientation $\theta=54\cdot6°$, $\varphi=163\cdot2°$ using $|F(h)|^2$ is shown in Fig. 2. Rotating the point vector set of the chlorine plus seven carbon atoms gave a best fit in the position shown.

Weighted β-modified coefficients according to the expression

$$\beta_h=\left\{\left(\frac{|F_o|^2-|F_p|^2-\Sigma f_Q^2}{|F_p|}\right)\exp i\alpha_p\right\}\tanh\frac{|F_o|\ |F_p|}{\Sigma f_Q^2},$$

F_p being for the chlorine +7 carbon atoms and the Σf_Q being over the 7 carbon +1 oxygen atom (Ramachandran, 1964) were used to compute a Fourier synthesis which revealed the position of the second ring and exocyclic acetyl group.

A calculation of the plane of the second ring indicated a normal at $\theta=88°$, $\varphi=23°$ which is close to the small peak on the $I(\theta,\varphi)$ function (Fig. 1). A preliminary value for the angle between the planes of the rings was 50°.

Coordinates were extracted from the β-synthesis and on the basis of 1 chlorine +15 carbon atoms the three-dimensional structure factors had a residual of 33%.

Refinement

The structure was refined by three cycles of Fourier refinement to $R=24\%$. A bond scan on the acetyl group indicated the oxygen atom and the inclusion of this in the structure factor calculation together with an adjustment to the overall thermal parameters resulted in a residual of 21%. Three cycles of refinement by the block-diagonal least-squares program (for the Elliot 803-B computer) of Daly, Stephens & Wheatley (1963) using partial shifts of 0·8 and individual isotropic thermal parameters reduced the residual to 15%. Two further cycles using anisotropic thermal parameters defined as

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

resulted in a residual of 11·8%.

A three-dimensional difference Fourier synthesis based on the structure factors from the last cycle of least-squares refinement showed the positions of the eight hydrogen atoms attached to the benzene rings together with three regions of 0·5 to 0·7 e.Å^{-3} around the methyl carbon atom. A projection of this map along the a axis is shown in Fig. 3. Coordinates for the eight hydrogen atoms attached to the biphenyl rings were calculated on the assumption of their planarity with the phenyl ring to which they were attached and a C–H bond length of 1·08 Å. The coordinates of the methyl hydrogen atoms were allocated on the basis of the C–C–H bond angles being 110°.

Refinement was continued with the program of Cruickshank *et al*, (1961) on the Leeds KDF9 computer and proceeded to a residual of 11%. The weighting scheme used was

$$\sqrt{w}=1/\left\{2|F_{\min}|+|F_o|+\frac{2|F_o|^2}{|F_{\max}|}+\frac{5|F_o|^3}{|F_{\max}|^2}\right\}^{1/2}.$$

At this stage of the refinement the reflexions 100, $11\bar{1}$, $13\bar{1}$, and 150 were excluded as it was suspected that these suffered from extinction. A final residual of 9·7% was obtained.

The final structure factors are given in Table 1, those reflexions which were not observed, either from 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 on Table 4.

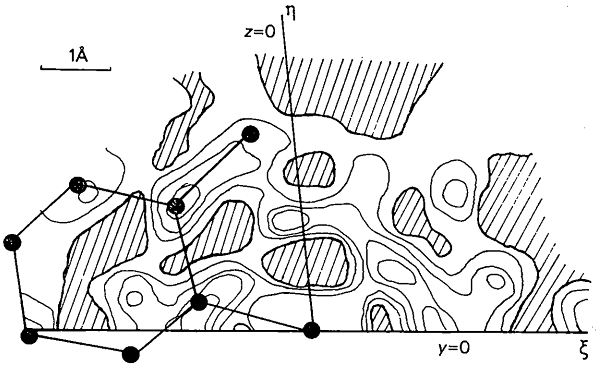

Fig. 2. Patterson projection in the plane perpendicular to $\theta=54\cdot6°$, $\varphi=163\cdot2°$.

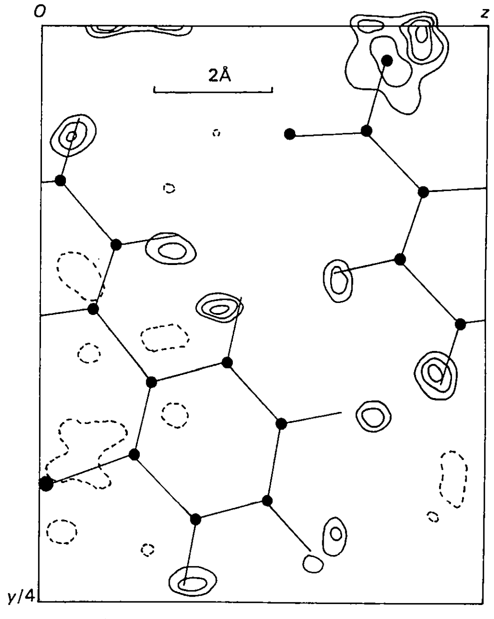

Fig. 3. Composite (yz) projection of the difference Fourier synthesis at $R=11\cdot8\%$. Intervals at 0·1 e.Å^{-3} starting at 0·3 e.Å^{-3}. Broken contours indicate regions of about 0·3 e.Å^{-3} occurring between two molecules.

Table 1. *Observed and calculated structure factors*

The table is in groups of *hkl* $100F_o$, and $100F_c$. An asterisk denotes an unobserved reflexion.

0	2	0	•	-2340
0	4	0	4214	-4043
0	6	0	2807	2277
0	8	0	6584	-7041
0	10	0	5724	5139
0	12	0	7081	-6942
0	14	0	6018	5785
0	16	0	875	538
0	18	0	947	-1046
0	20	0	4917	5087
0	22	0	2830	-3013
0	24	0	2328	2224
0	26	0	1452	-1115
0	28	0	1031	-865
0	30	0	2136	2178
0	32	0	1529	-1577
0	34	0	•	-528
0	36	0	3338	-3286
0	38	0	•	-540
0	40	0	1961	1912
0	42	0	•	-1009
0	44	0	•	392
0	1	1	4260	4100
0	2	1	2601	-2223
0	3	1	2679	-2097
0	4	1	9137	8840
0	5	1	3132	-2554
0	6	1	2310	2176
0	7	1	3742	-3354
0	8	1	3226	2870
0	9	1	5957	5297
0	10	1	876	732
0	11	1	3160	3046
0	12	1	1782	1550
0	13	1	2476	-2267
0	14	1	•	262
0	15	1	6651	6793
0	16	1	2132	-2389
0	17	1	2165	-2297
0	18	1	2364	2172
0	19	1	2078	-1916
0	20	1	1322	1091
0	21	1	1225	-1331
0	22	1	•	92
0	23	1	2073	-2434
0	24	1	1068	1151
0	25	1	2315	2672
0	26	1	•	477
0	27	1	1999	-2415
0	28	1	•	30
0	29	1	1774	1870
0	30	1	2008	2117
0	31	1	1923	2005
0	32	1	1399	1631
0	33	1	1636	-1189
0	34	1	1204	-1285
0	35	1	•	-440
0	36	1	•	-235
0	37	1	1865	-2093
0	38	1	•	-116
0	39	1	1260	1710
0	40	1	•	1
0	41	1	•	-473
0	42	1	•	15
0	43	1	•	-248
0	44	1	•	-252
0	45	1	•	1123
0	0	2	4390	4213
0	1	2	673	-587
0	2	2	6329	-5681
0	3	2	735	-759
0	4	2	714	588
0	5	2	1554	-1445
0	6	2	•	-207
0	7	2	2804	-2524
0	8	2	5814	-5435
0	9	2	2572	2287
0	10	2	940	1037
0	11	2	666	-631
0	12	2	6172	-6233
0	13	2	•	-169
0	14	2	4514	4280
0	15	2	4031	4011
0	16	2	3054	2919
0	17	2	1331	1169
0	18	2	1695	-1507
0	19	2	1047	1054
0	20	2	•	340
0	21	2	•	392
0	22	2	3259	-3343
0	23	2	•	402
0	24	2	2943	3218
0	25	2	1443	-1407
0	26	2	1630	-1653
0	27	2	1251	-1092
0	28	2	1000	-572
0	29	2	1679	1808
0	30	2	2182	2980
0	31	2	•	95
0	32	2	2274	-2480
0	33	2	•	415
0	34	2	2522	2573
0	35	2	•	-511
0	36	2	•	54
0	37	2	•	-65
0	38	2	•	-659
0	39	2	•	445
0	40	2	1375	1596
0	41	2	•	-150
0	42	2	1042	-972
0	43	2	•	411
0	44	2	1083	1399
0	45	2	•	-547
0	1	3	3291	-2600
0	2	3	666	504
0	3	3	1799	-1704
0	4	3	1595	-1263
0	5	3	4532	4295
0	6	3	•	107
0	7	3	3073	-2780
0	8	3	2003	1943
0	9	3	1114	937
0	10	3	3178	-3044
0	11	3	3103	-2724
0	12	3	833	-602
0	13	3	959	-945
0	14	3	•	13
0	15	3	3220	3309
0	16	3	1745	-1832
0	17	3	2368	-2352
0	18	3	1126	953
0	19	3	1047	1203
0	20	3	981	-1030
0	21	3	1093	-955
0	22	3	•	84
0	23	3	•	-717
0	24	3	•	-161
0	25	3	1837	2134
0	26	3	•	-258
0	27	3	1126	-941
0	28	3	•	472
0	29	3	1251	1161
0	30	3	1573	-1721
0	31	3	•	-684
0	32	3	•	147
0	33	3	•	100
0	34	3	•	-140
0	35	3	1417	1596
0	36	3	•	-890
0	37	3	•	-920
0	38	3	•	635
0	39	3	•	690
0	0	4	3419	3062
0	1	4	1923	-1671
0	2	4	2625	-2561
0	3	4	•	-7
0	4	4	2671	2443
0	5	4	3294	-3366
0	6	4	2542	2571
0	7	4	1620	-1668
0	8	4	3904	-3957
0	9	4	2023	2034
0	10	4	2255	2183
0	11	4	•	-580
0	12	4	1611	-1908
0	13	4	•	745
0	14	4	•	68
0	15	4	•	-417
0	16	4	•	21
0	17	4	•	536
0	18	4	1042	-940
0	19	4	1546	-1553
0	20	4	3138	3218
0	21	4	1769	-1918
0	22	4	2276	-2338
0	23	4	1382	1383
0	24	4	1126	843
0	25	4	1209	-903
0	26	4	•	492
0	27	4	•	777
0	28	4	1335	-1304
0	29	4	•	-540
0	30	4	1527	955
0	31	4	1768	-1552
0	32	4	1417	-1618
0	33	4	•	901
0	34	4	•	996
0	35	4	•	-582
0	1	5	876	963
0	2	5	•	30
0	3	5	1133	-1331
0	4	5	1032	901
0	5	5	1799	2014
0	6	5	•	-343
0	7	5	1375	-1489
0	8	5	959	803
0	9	5	•	640
0	10	5	1417	1623
0	11	5	1562	1828
0	12	5	959	709
0	13	5	•	-907
0	14	5	•	-360
0	15	5	•	608
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0	20	5	1126	-987
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0	28	5	•	-169
0	29	5	•	287
0	30	5	•	-830
0	0	6	•	723
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0	3	6	•	524
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0	5	6	1626	-1549
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0	7	6	2385	-2552
0	8	6	1620	-1572
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0	10	6	3481	3795
0	11	6	•	687
0	12	6	•	-588
0	13	6	1417	1387
0	14	6	•	377
0	15	6	•	-290
0	1	7	•	509
0	2	7	•	402
0	3	7	•	117
0	4	7	•	-307
0	5	7	•	16
0	6	7	1335	-1775
0	7	7	•	-773
0	8	7	1417	1601
0	9	7	•	-842
0	10	7	•	262
1	0	0	6201	8737
1	1	0	334	-216
1	2	0	307	30
1	3	0	3576	3881
1	4	0	4517	-5182
1	5	0	8358	10537
1	6	0	5395	-6065
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1	8	0	839	-768
1	9	0	4720	-5465
1	10	0	3523	3641
1	11	0	1557	1592
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1	15	0	1516	-1683
1	16	0	1260	937
1	17	0	1490	1336
1	18	0	1707	-1767
1	19	0	1110	-1225
1	20	0	1182	992
1	21	0	2985	2833
1	22	0	•	-525
1	23	0	1092	-1152
1	24	0	•	311
1	25	0	1503	1236
1	26	0	•	283
1	27	0	1004	939
1	28	0	•	-293
1	29	0	1064	-895
1	30	0	1729	1807
1	31	0	3266	3657
1	32	0	1551	1460
1	33	0	1262	-1316
1	34	0	1342	-1130
1	35	0	1064	667
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1	37	0	•	281
1	38	0	1078	943
1	39	0	1368	-1700
1	40	0	986	873
1	41	0	•	452
1	42	0	•	-25
1	43	0	923	-1133
1	44	0	•	414
1	45	0	1100	1572
1	1	1	1344	1473
1	2	1	2167	1978
1	3	1	6186	-6773
1	4	1	2158	-2254
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1	8	1	5187	-5588
1	9	1	2356	2448
1	10	1	910	-805
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1	12	1	748	-544
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1	14	1	1712	-1332
1	15	1	2211	2453
1	16	1	4239	4658
1	17	1	1015	-534
1	18	1	2759	-3112
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1	24	1	3168	-3369
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1	36	1	1572	1674
1	37	1	1477	-1175
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1	39	1	1301	1293
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1	41	1	•	256
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1	2	-1	5165	6061
1	3	-1	5599	-7295
1	4	-1	8219	-9399
1	5	-1	3382	3459
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1	10	-1	963	-877
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1	12	-1	2369	2190
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1	34	-1	•	191
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1	2	2	833	805
1	3	2	2970	-3031
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1	5	2	1554	1547
1	6	2	973	-714
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1	8	2	•	288
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1	10	2	1421	-1423
1	11	2	920	-658
1	12	2	3964	-4135
1	13	2	2202	-2579
1	14	2	2925	3012
1	15	2	•	177
1	16	2	•	150
1	17	2	•	-119
1	18	2	•	-118
1	19	2	•	-535
1	20	2	824	873
1	21	2	2544	2714
1	22	2	•	-632
1	23	2	2564	-2423
1	24	2	1805	1521
1	25	2	1467	-1161
1	26	2	1345	-1250
1	27	2	1128	-727
1	28	2	•	-238
1	29	2	1388	-1038
1	30	2	•	188
1	31	2	1594	1405
1	32	2	1171	-916
1	33	2	1301	-1145
1	34	2	•	832
1	35	2	•	-114
1	0	-2	6770	-7748
1	1	-2	4080	4415
1	2	-2	3341	3341
1	3	-2	1518	-1166
1	4	-2	3082	2809
1	5	-2	•	-264
1	6	-2	•	118
1	7	-2	2634	2601
1	8	-2	2592	2268
1	9	-2	3278	-3466
1	10	-2	771	670
1	11	-2	1885	1996
1	12	-2	867	762
1	13	-2	3302	-3192
1	14	-2	1567	1397
1	15	-2	652	477
1	16	-2	3489	3639
1	17	-2	1439	1319
1	18	-2	1409	-1076
1	19	-2	3130	-3187
1	20	-2	3276	-2795
1	21	-2	3692	3668
1	22	-2	1594	-1222
1	23	-2	1650	-1490
1	24	-2	1371	854
1	25	-2	1086	-734
1	26	-2	•	665
1	27	-2	•	1245
1	28	-2	1345	-1127
1	29	-2	1784	-1790
1	30	-2	1258	760
1	31	-2	•	-80
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Table 1 (*cont.*)

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3	25	1	1183	-1311
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3	27	1	•	296
3	28	1	•	213
3	29	1	799	-789
3	30	1	685	698
3	31	1	•	161
3	32	1	•	-530
3	33	1	•	249
3	34	1	•	445
3	35	1	•	-345
3	36	1	•	-254
3	37	1	744	818
3	38	1	•	97
3	39	1	•	-718
3	1	-1	772	-995
3	2	-1	607	-614
3	3	-1	490	523
3	4	-1	1143	1314
3	5	-1	434	-410
3	6	-1	•	167
3	7	-1	1727	2020
3	8	-1	826	684
3	9	-1	614	-515
3	10	-1	1488	-1509
3	11	-1	648	526
3	12	-1	704	-707
3	13	-1	•	189
3	14	-1	767	737
3	15	-1	1456	-1292
3	16	-1	657	-627
3	17	-1	1899	2163
3	18	-1	523	503
3	19	-1	1635	-1664
3	20	-1	947	-761
3	21	-1	•	-139
3	22	-1	•	-363
3	23	-1	815	740
3	24	-1	•	182
3	25	-1	1014	-713
3	26	-1	1046	-869
3	27	-1	1158	1085
3	28	-1	•	215
3	29	-1	1708	-1606
3	30	-1	•	452
3	31	-1	•	320
3	32	-1	•	-353
3	33	-1	•	356
3	34	-1	•	-274
3	35	-1	•	-607
3	36	-1	•	475
3	37	-1	1290	1085
3	38	-1	•	293
3	39	-1	643	-843
3	40	-1	744	-1046
3	0	2	1985	-2080
3	1	2	866	-889
3	2	2	691	578
3	3	2	•	141
3	4	2	806	-575
3	5	2	•	174
3	6	2	•	95
3	7	2	647	560
3	8	2	1359	1581
3	9	2	•	496
3	10	2	1568	-1664
3	11	2	594	-734
3	12	2	1191	1186
3	13	2	1037	917
3	14	2	•	-391
3	15	2	672	-612
3	16	2	1686	-1676
3	17	2	758	-740
3	18	2	•	413
3	19	2	•	-258
3	20	2	•	229
3	21	2	•	105
3	22	2	1129	1159
3	23	2	869	988
3	24	2	881	-956
3	25	2	778	-816
3	26	2	•	244
3	27	2	•	-178
3	28	2	•	585
3	29	2	747	871
3	30	2	1078	-1198
3	31	2	•	47
3	32	2	903	1079
3	33	2	•	14
3	34	2	•	75
3	0	-2	1190	-1109
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3	2	-2	365	252
3	3	-2	•	109
3	4	-2	•	-125
3	5	-2	964	952
3	6	-2	561	543
3	7	-2	415	-403
3	8	-2	402	455
3	9	-2	•	217
3	10	-2	1911	-2397
3	11	-2	586	-497
3	12	-2	•	164
3	13	-2	•	163
3	14	-2	553	343
3	15	-2	964	-957
3	16	-2	•	-64
3	17	-2	•	80
3	18	-2	601	523
3	19	-2	1073	884
3	20	-2	1284	-1269
3	21	-2	1505	-1366
3	22	-2	•	356
3	23	-2	706	384
3	24	-2	•	56
3	25	-2	818	-635
3	26	-2	1181	1290
3	27	-2	•	269
3	28	-2	•	120
3	29	-2	924	729
3	30	-2	1786	-1642
3	31	-2	1178	-1280
3	32	-2	967	1221
3	33	-2	1244	1098
3	34	-2	•	-521
3	35	-2	774	-558
3	36	-2	•	36
3	37	-2	•	-167
3	38	-2	646	592
3	39	-2	603	669
3	40	-2	•	-285
3	1	3	1276	-1235
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3	4	3	747	-413
3	5	3	850	-624
3	6	3	1068	899
3	7	3	1312	1302
3	8	3	856	-527
3	9	3	1409	-1332
3	10	3	•	243
3	11	3	•	738
3	12	3	•	245
3	13	3	760	821
3	14	3	909	-777
3	15	3	1054	-1220
3	16	3	•	-147
3	17	3	1185	1359
3	18	3	•	132
3	19	3	1143	-1209
3	20	3	•	193
3	21	3	•	207
3	22	3	•	-654
3	23	3	•	150
3	24	3	•	41
3	25	3	669	-841
3	26	3	•	-109
3	27	3	685	825
3	28	3	•	-291
3	1	-3	832	-851
3	2	-3	1185	1360
3	3	-3	1599	1736
3	4	-3	1090	-971
3	5	-3	1800	-2360
3	6	-3	1668	-1945
3	7	-3	1915	2421
3	8	-3	1860	2133
3	9	-3	1739	-1944
3	10	-3	546	365
3	11	-3	738	-764
3	12	-3	566	-642
3	13	-3	1417	1556
3	14	-3	678	674
3	15	-3	1524	-1525
3	16	-3	1018	-837
3	17	-3	1241	1306
3	18	-3	706	649
3	19	-3	985	-1020
3	20	-3	•	135
3	21	-3	•	-48
3	22	-3	•	64
3	23	-3	•	514
3	24	-3	•	462
3	25	-3	•	-140
3	26	-3	•	-498
3	27	-3	1306	1315
3	28	-3	1126	987
3	29	-3	719	-674
3	30	-3	617	-604
3	31	-3	•	-125
3	32	-3	•	-312
3	33	-3	•	132
3	34	-3	583	622
3	35	-3	•	-99
3	36	-3	509	-604
3	37	-3	•	257
3	38	-3	•	285
3	39	-3	•	-119
3	0	4	1185	-939
3	1	4	•	93
3	2	4	811	645
3	3	4	•	-108
3	4	4	•	397
3	5	4	•	-489
3	6	4	•	-314
3	7	4	•	-232
3	8	4	•	293
3	9	4	•	560
3	10	4	•	-582
3	11	4	•	-470
3	12	4	•	351
3	13	4	•	-554
3	14	4	•	190
3	15	4	•	529
3	16	4	•	430
3	17	4	•	217
3	18	4	•	241
3	19	4	•	485
3	20	4	939	-1081
3	21	4	•	-298
3	22	4	647	731
3	23	4	•	-250
3	24	4	•	-534
3	0	-4	1742	-1586
3	1	-4	2279	-2144
3	2	-4	1090	1056
3	3	-4	1348	1449
3	4	-4	1063	904
3	5	-4	1341	-1041
3	6	-4	1800	-1612
3	7	-4	2146	-2126
3	8	-4	•	345
3	9	-4	2882	3006
3	10	-4	917	766
3	11	-4	•	-193
3	12	-4	826	846
3	13	-4	795	788
3	14	-4	1030	-784
3	15	-4	1143	-859
3	16	-4	727	-488
3	17	-4	•	-178
3	18	-4	1294	1185
3	19	-4	1145	1143
3	20	-4	895	-843
3	21	-4	1183	-999
3	22	-4	777	778
3	23	-4	992	979
3	24	-4	•	17
3	25	-4	•	256
3	26	-4	983	-998
3	27	-4	•	326
3	28	-4	865	721
3	29	-4	•	-237
3	30	-4	•	-57
3	31	-4	882	-814
3	32	-4	•	5
3	33	-4	583	923
3	34	-4	•	-457
3	35	-4	•	-409
3	36	-4	•	345
3	37	-4	•	-347
3	1	5	•	422
3	2	5	•	467
3	3	5	•	595
3	4	5	961	654
3	5	5	•	-893
3	6	5	778	-150
3	7	5	•	842
3	8	5	•	-161
3	9	5	•	-724
3	10	5	•	116
3	11	5	•	-443
3	12	5	•	-430
3	13	5	•	619
3	14	5	•	-112
3	15	5	•	-323
3	16	5	•	390
3	17	5	604	705
3	18	5	•	177
3	19	5	594	-599
3	20	5	•	378
3	21	5	•	-8
3	1	-5	•	9
3	2	-5	759	-504
3	3	-5	•	589
3	4	-5	803	627
3	5	-5	1334	-1120
3	6	-5	1641	-1420
3	7	-5	888	787
3	8	-5	•	311
3	9	-5	•	101
3	10	-5	1720	1530
3	11	-5	1035	1001
3	12	-5	•	39
3	13	-5	•	718
3	14	-5	•	50
3	15	-5	1674	-1662
3	16	-5	1739	-1488
3	17	-5	•	-100
3	18	-5	930	883
3	19	-5	•	15
3	20	-5	•	-456
3	21	-5	1490	1396
3	22	-5	1558	-1643
3	23	-5	605	-359
3	24	-5	1911	2195
3	25	-5	1417	-1647
3	26	-5	•	166
3	27	-5	977	1201
3	28	-5	•	-488
3	29	-5	•	-376
3	0	6	•	-369
3	1	6	783	781
3	2	6	621	621
3	3	6	652	835
3	4	6	615	-683
3	5	6	•	248
3	6	6	•	-417
3	7	6	•	-100
3	8	6	647	802
3	9	6	•	-122
3	0	-6	•	-21
3	1	-6	1046	-930
3	2	-6	•	-62
3	3	-6	1008	892
3	4	-6	•	-2
3	5	-6	924	-861
3	6	-6	770	701
3	7	-6	•	-792
3	8	-6	722	-625
3	9	-6	1611	1629
3	10	-6	•	-203
3	11	-6	•	-728
3	12	-6	1030	1065
3	13	-6	•	265
3	14	-6	1209	-995
3	15	-6	•	-574
3	16	-6	722	-739
3	17	-6	•	303
3	18	-6	•	192
3	19	-6	•	-265
3	20	-6	810	753
3	21	-6	1328	-1613
3	22	-6	•	293
3	23	-6	1124	1328
3	24	-6	561	-682
3	25	-6	•	-56
3	1	-7	883	-949
3	2	-7	•	106
3	3	-7	665	716
3	4	-7	•	-150
3	5	-7	•	-73
3	6	-7	803	-828
3	7	-7	655	553
3	8	-7	910	822
3	9	-7	•	-395
3	10	-7	673	-543
3	11	-7	627	-684
3	12	-7	•	35
3	13	-7	744	776
3	14	-7	793	679
3	15	-7	•	-348
3	16	-7	605	-580
3	17	-7	•	42
3	18	-7	601	516
3	19	-7	•	-134
3	20	-7	527	-700
3	21	-7	•	-108
3	6	-8	•	-41
3	7	-8	•	-364
3	8	-8	•	243
3	9	-8	686	799
3	10	-8	496	-446
3	11	-8	624	-683
3	12	-8	•	-256
3	13	-8	•	393

Table 2. *The final coordinates* (Å) *for the non-hydrogen atoms*

	X	*Y*	*Z*
Cl(1)	−0·7563	7·8094	0·1261
C(1)	0·6774	5·9402	1·8608
C(2)	0·2894	7·3157	1·6197
C(3)	0·7074	8·2523	2·6200
C(4)	1·5230	7·9319	3·8363
C(5)	1·8812	6·6049	4·0934
C(6)	1·4614	5·6344	3·0934
C(7)	0·2565	4·8681	0·8387
C(8)	0·4497	4·9971	−0·4983
C(9)	0·0799	3·9527	−1·4290
C(10)	−0·4989	2·7766	−1·0128
C(11)	−0·6375	2·6634	0·3170
C(12)	−0·2827	3·6762	1·2432
C(13)	−0·9333	1·6849	−2·0411
C(14)	−1·4129	0·4825	−1·6085
O(1)	−0·9595	1·9490	−3·3162

Discussion

The arrangement of the molecules in the unit cell viewed along the *a* axis is shown in Fig. 4. The packing is different from that found in 4-acetyl-2′-fluorobiphenyl (Young, Tollin & Sutherland, 1968) in that the molecules are related across a centre of symmetry with the acetyl group of one molecule facing the acetyl group of the symmetry related molecule. There is however no evidence from the van der Waals contacts of any bonding. All contacts of less than 3·7 Å are given in Table 5, the intramolecular bond lengths and angles being shown in Fig. 5.

The equations for the mean planes of the ring systems C(1)–C(6), C(1)–C(6)+Cl, C(7)–C(12), and the acetyl radical were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) with respect to the orthogonal triad **a**, **b**, **c***. The equations together with the deviations of the atoms from the planes are given in Table 6. The angle between the acetyl radical and the phenyl ring C(7)–C(12) is 7·9° and the angle between the two phenyl rings 49·2°. The value of 56·4° predicted by Branch, Byron, Gray, Ibbotson & Worral (1964), using a simple mathematical treatment on non-sterically affected molecules rotating about the biphenyl bond until the 2 and 2′ atoms are separated by the sum of their van der Waals radii, indicates that some steric effects are present. The value of 49·2° is in good agreement with the values of 48·9° for 2′-chlorobiphenyl-4-carboxylic acid (Sutherland, 1967) and 46·1° for 2-chlorobiphenyl-4-carboxylic acid (Sutherland & Hoy, 1967).

Table 4. *Idealized hydrogen coordinates (Å)*

H(3)	0·3939	9·2399	2·4485
H(4)	1·8847	8·7171	4·5923
H(5)	2·4854	6·3170	5·0666
H(6)	1·7558	4·6436	3·2937
H(8)	0·8858	5·9038	−0·8225
H(9)	0·2408	4·0535	−2·4683
H(11)	−1·0301	1·7758	0·6421
H(12)	−0·4216	3·5492	2·2866
H(14)	−2·1804	0·7181	−1·0620
H(15)	−0·5945	0·0189	−0·9923
H(16)	−1·7606	−0·0818	−2·4787

Table 5. *Intermolecular distances between atoms less than* 3·7 Å

i	*j*	Equipoint indication	d_{ij}
Cl(1)	C(2)	$x+1, y, z$	3·572
C(6)	C(1)	$x+1, y, z$	3·654
C(8)	C(12)	$x+1, y, z$	3·668
C(9)	C(11)	$x+1, y, z$	3·670
C(10)	C(9)	$x+1, y, z$	3·572
C(12)	C(7)	$x+1, y, z$	3·615
C(12)	O(1)	$x, y, z+1$	3·593
C(4)	C(3)	$x+1, y, z+1$	3·617

The distance of 1·738 Å for the carbon–chlorine bond obtained in this analysis is considerably longer than the value published in Volume III of *International Tables for X-ray Crystallography* of 1·70 ± 0·01 Å. In *o*-chlorobenzoic acid, Ferguson & Sim (1961) the Cl–C distance was determined as 1·737 Å, in good agreement with the value found in the present analysis. The C(1)–C(7) bond length of 1·490 Å lies between the values of 1·506 ± 0·017 Å for biphenyl (Trotter, 1961) and 1·479 ± 0·010 Å for 4-acetyl-2′-fluorobiphenyl (Young, Tollin & Sutherland, 1968), being significantly shorter than the quoted value of 1·54 Å. It is, however,

Table 3. *Thermal parameters* (Å²) *for non-hydrogen atoms*

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl(1)	0·0522	0·0301	0·0488	0·0176	0·0252	0·0266
C(1)	0·0341	0·0247	0·0404	−0·0007	−0·0198	0·0544
C(2)	0·0335	0·0402	0·0393	−0·0136	−0·0242	0·0460
C(3)	0·0454	0·0434	0·0495	0·0081	0·0049	0·0274
C(4)	0·0445	0·0757	0·0486	−0·0368	−0·0563	0·0510
C(5)	0·0510	0·0614	0·0557	0·0178	0·0144	0·0418
C(6)	0·0355	0·0469	0·0452	0·0030	−0·0088	0·0273
C(7)	0·0110	0·0343	0·0357	0·0183	0·0038	0·0189
C(8)	0·0494	0·0359	0·0263	−0·0052	−0·0230	0·0429
C(9)	0·0441	0·0394	0·0506	0·0064	0·0029	0·0465
C(10)	0·0375	0·0297	0·0410	−0·0010	−0·0202	−0·0010
C(11)	0·0571	0·0339	0·0303	−0·0153	0·0240	0·0099
C(12)	0·0410	0·0396	0·0358	−0·0205	−0·0073	0·0206
C(13)	0·0650	0·0609	0·0698	−0·0429	−0·0251	−0·0232
C(14)	0·0970	0·0228	0·0803	−0·0233	−0·0004	0·0226
O(1)	0·2031	0·1135	0·0543	−0·0903	−0·0200	0·0365

Table 6. *Equations of the mean planes*

The equations for the mean planes of the ring systems (i) C(1)–C(6), (ii) C(1)–C(6)+Cl (iii) C(7)–C(12) and (iv) the acetyl radical are:

(i)	$+0{\cdot}9067X$	$+0{\cdot}1596Y$	$-0{\cdot}3905Z$	=	$+0{\cdot}5464$	$\theta=57°$	$\varphi=169°$
(ii)	$+0{\cdot}9012X$	$+0{\cdot}1632Y$	$-0{\cdot}4016Z$	=	$+0{\cdot}5331$	$\theta=56{\cdot}3$	$\varphi=168{\cdot}7$
(iii)	$-0{\cdot}8910X$	$+0{\cdot}3867Y$	$-0{\cdot}2379Z$	=	$+1{\cdot}5822$	$\theta=85{\cdot}5$	$\varphi=22{\cdot}8$
(iv)	$-0{\cdot}9275X$	$+0{\cdot}3578Y$	$-0{\cdot}1083Z$	=	$+1{\cdot}3811$		

Deviations from the mean planes in (Å).

	(i)	(ii)		(iii)		(iv)
Cl(1)	....	−0·008	C(7)	0·007	C(10)	0·005
C(1)	0·003	0·015	C(8)	−0·010	C(13)	−0·025
C(2)	0·008	0·030	C(9)	0·006	C(14)	0·007
C(3)	−0·018	−0·005	C(10)	0·003	O(1)	0·009
C(4)	+0·018	0·013	C(11)	−0·006		
C(5)	−0·009	−0·023	C(12)	0·001		
C(6)	−0·002	−0·007				

only possibly significantly over the theoretical values of Dewar & Schmeising (1959) and Cruickshank & Sparks (1960), who suggest that the (sp^2) single-bond length between trigonally linked carbons should be taken as 1·477 Å.

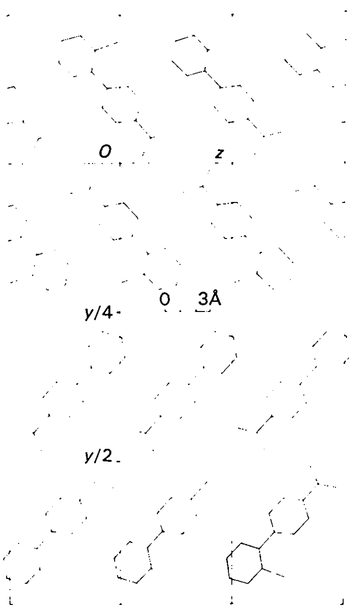

Fig. 4. Packing of the molecules in the (*yz*) projection.

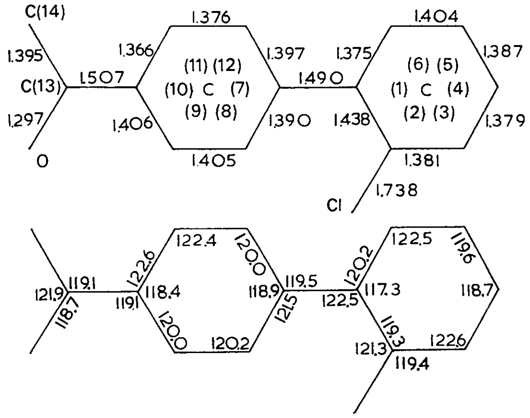

Fig. 5. Bond lengths and angles. Bond lengths are in Å ±0·010 Å. Angles are in degrees ±1·0°.

The C(1)–C(2) bond length of 1·44 Å is significantly longer than the quoted value of 1·40±0·01 Å and the value of 1·405 Å obtained for *o*-chlorobenzoic acid.

A peculiar feature of the acetyl group is the C(13)–C(14) bond length of 1·40 Å and C(13)–O of 1·30 Å, which are considerably different from the quoted values of 1·50 and 1·23 Å respectively.

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