

The Crystal Structure of 2'-Iodobiphenyl-4-carboxylic Acid

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The crystal structure of 2'-iodobiphenyl-4-carboxylic acid, $C_{13}H_9O_2I$, has been determined from three-dimensional X-ray diffraction data. The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 4.15$, $b = 7.73$, $c = 17.79$ Å, $\alpha = 99^\circ 4'$, $\beta = 91^\circ 23'$, $\gamma = 97^\circ 34'$. The structure, which consists of centrosymmetrical hydrogen-bonded dimers, was refined by block-diagonal least-squares refinement with anisotropic thermal parameters to a residual of 9% for the 1758 observed structure factors. The angle between the two phenyl rings and the angle between the carboxyl group and the phenyl ring to which it is attached were found to be 51.3 and 5.2° respectively.

Introduction

X-ray analyses of several simple derivatives of biphenyl with 2 and 2' fluorine or chlorine substitutions have been shown to have interplanar angles of around 48° . As biphenyl in the solid phase is planar (Dhar, 1932; Trotter, 1961; Hargreaves & Rizvi, 1962) it was of interest to determine the interplanar angle with iodine in the 2' substituted position as this angle would be expected to be greater than that obtained for the chlorine derivatives. This paper describes the crystal and molecular structure of 2'-iodobiphenyl-4-carboxylic acid, the sixth in a series of related compounds being investigated by the author.

Experimental

2'-Iodobiphenyl-4-carboxylic acid was crystallized from toluene, producing transparent platelets. The observed density at 17°C was measured by the method of flotation using aqueous cadmium n-dodecatungstoborate.

Crystal data

$C_{13}H_9O_2I$	$M = 324.1$	triclinic
$a = 4.15 \pm 0.01$	$b = 7.73 \pm 0.01$	$c = 17.79 \pm 0.02$ Å
$\alpha = 99^\circ 4' \pm 5'$	$\beta = 91^\circ 23' \pm 5'$	$\gamma = 97^\circ 34' \pm 5'$
$U = 558.1$ Å ³	$D_m = 1.90$ g.cm ⁻³	$D_c = 1.93$ g.cm ⁻³
$Z = 2$	$F(000) = 312$	Cu $K\alpha$ ($\lambda = 1.5418$ Å)

No absent spectra: space group $P\bar{1}$ (no. 2)

In order to minimize absorption effects a crystal of approximately square cross section was chosen for intensity data collection about the a axis. Data for the $0kl, 1kl, 2kl, 3kl$ and $h0l$ levels of reciprocal space were collected by the multiple-film equi-inclination Weissenberg technique, using Cu $K\alpha$ radiation. The $h0l$ intensity data were collected using a crystal cut from one of the platelets.

Intensities of the spots were measured on a Joyce-Loebl Flying Spot Densitometer. The data were brought to the same arbitrary scale and finally on to an approximately absolute scale by applying the method of Wilson (1942) to the $0kl$ level.

Determination and refinement of the structure

The $0kl$ projection of the unit cell was solved from the sharpened Patterson projection and refined by a combination of electron density distribution and block-diagonal least-squares to a residual of $R = 0.10$ where $R = \sum |F_o| - |F_c| / \sum |F_o|$. The calculations were carried out on an Elliot 803B computer using the programs of Daly, Stephens & Wheatley (1963).

The $h0l$ projection of the Patterson function gave provisional x coordinates for the atoms.

A structure factor calculation using full three-dimensional data gave a residual of $R = 0.22$. For this the average value of $F(hkl)$ and $F(\bar{h}\bar{k}\bar{l})$ was used. The scattering factor for iodine was taken to be $f = \{(f_0 + f'')^2 + \Delta f''^2\}^{1/2}$ where f_0 is the scattering factor appropriate to a wavelength far from an absorption edge, f' is the real part of the correction due to anomalous scattering and $\Delta f''$ is the imaginary part of the correction term. Due to the poor quality of the crystals it was decided to use this throughout this investigation.

The structure was refined by two cycles of three-dimensional electron density distributions and structure factor calculations and thereafter by block-diagonal least squares applied to positional parameters, overall scale factor and individual isotropic thermal parameters, to a residual of $R = 0.13$. After three cycles incorporating anisotropic thermal parameters defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), a three-dimensional difference electron density distribution was calculated; this showed regions of density at the positions where the eight hydrogen atoms attached to the phenyl rings would be expected and a region of density between the oxygen atoms involved in the hydrogen bonding indicating that the hydrogen was probably attached to O(1).

During the subsequent refinement 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). Individual scale factors for the batches of data were included in the refinement and a weighting scheme,

tion were calculated. Apart from slight regions of density between the iodine atoms, there were no unusual features. The final structure factors are given in Table 1, those reflexions which were not observed in the region

of reciprocal space examined are marked with an asterisk. The 001 and the 1 $\bar{1}$ 0 reflexions were unobserved because of the camera geometry on the *a*-axis Weissenberg photographs. An estimate of the 1 $\bar{1}$ 0 reflexion

Table 1 (cont.)

H	K	L	100F0	100F0*	H	K	L	100F0	100F0*	H	K	L	100F0	100F0*
1	1	-19	2419	996	1	4	5	2200	1920	2	-1	2	2544	2223
1	1	-18	2914	-258	1	4	10	3278	-2940	2	-1	7	1532	1955
1	1	-17	2988	1996	1	4	15	3728	3241	2	-1	10	1820	2518
1	1	-16	3133	2857	1	4	20	4286	-1990	2	-1	13	2108	3104
1	1	-15	3773	-3144	1	4	25	4951	210	2	-1	16	2400	3720
1	1	-14	4288	3996	1	4	30	5630	-1859	2	-1	19	2700	4365
1	1	-13	4782	5377	1	4	35	6322	115	2	-1	22	3000	5025
1	1	-12	5252	-1337	1	4	40	7028	-1709	2	-1	25	3300	5700
1	1	-11	5702	2653	1	4	45	7748	1395	2	-1	28	3600	6390
1	1	-10	6132	6053	1	4	50	8482	-2316	2	-1	31	3900	7095
1	1	-9	6542	-1364	1	4	55	9230	102	2	-1	34	4200	7815
1	1	-8	6932	2654	1	4	60	10002	-1916	2	-1	37	4500	8550
1	1	-7	7302	-1012	1	4	65	10798	1316	2	-1	40	4800	9300
1	1	-6	7652	4183	1	4	70	11618	-2223	2	-1	43	5100	10065
1	1	-5	7982	-1012	1	4	75	12462	1167	2	-1	46	5400	10845
1	1	-4	8292	4107	1	4	80	13330	-2034	2	-1	49	5700	11640
1	1	-3	8582	-1344	1	4	85	14222	1364	2	-1	52	6000	12450
1	1	-2	8852	6457	1	4	90	15138	-2223	2	-1	55	6300	13275
1	1	-1	9102	-1012	1	4	95	16078	1167	2	-1	58	6600	14115
1	1	0	9332	4183	1	4	100	17042	-2034	2	-1	61	6900	14970
1	1	1	9542	-1344	1	4	105	18030	1364	2	-1	64	7200	15840
1	1	2	9732	6457	1	4	110	19042	-2223	2	-1	67	7500	16725
1	1	3	9902	-1012	1	4	115	20078	1167	2	-1	70	7800	17625
1	1	4	10052	4183	1	4	120	21138	-2034	2	-1	73	8100	18540
1	1	5	10182	-1344	1	4	125	22222	1364	2	-1	76	8400	19465
1	1	6	10292	6457	1	4	130	23330	-2223	2	-1	79	8700	20400
1	1	7	10382	-1012	1	4	135	24462	1167	2	-1	82	9000	21345
1	1	8	10452	4183	1	4	140	25618	-2034	2	-1	85	9300	22300
1	1	9	10502	-1344	1	4	145	26798	1364	2	-1	88	9600	23265
1	1	10	10532	6457	1	4	150	28002	-2223	2	-1	91	9900	24240
1	1	11	10542	-1012	1	4	155	29230	1167	2	-1	94	10200	25225
1	1	12	10532	4183	1	4	160	30482	-2034	2	-1	97	10500	26220
1	1	13	10492	-1344	1	4	165	31758	1364	2	-1	100	10800	27225
1	1	14	10422	6457	1	4	170	33058	-2223	2	-1	103	11100	28240
1	1	15	10322	-1012	1	4	175	34382	1167	2	-1	106	11400	29265
1	1	16	10192	4183	1	4	180	35730	-2034	2	-1	109	11700	30300
1	1	17	10032	-1344	1	4	185	37092	1364	2	-1	112	12000	31345
1	1	18	9842	6457	1	4	190	38468	-2223	2	-1	115	12300	32400
1	1	19	9622	-1012	1	4	195	39858	1167	2	-1	118	12600	33465
1	1	20	9372	4183	1	4	200	41262	-2034	2	-1	121	12900	34540
1	1	21	9092	-1344	1	4	205	42682	1364	2	-1	124	13200	35625
1	1	22	8782	6457	1	4	210	44118	-2223	2	-1	127	13500	36720
1	1	23	8442	-1012	1	4	215	45570	1167	2	-1	130	13800	37825
1	1	24	8072	4183	1	4	220	47038	-2034	2	-1	133	14100	38940
1	1	25	7672	-1344	1	4	225	48522	1364	2	-1	136	14400	40065
1	1	26	7242	6457	1	4	230	50022	-2223	2	-1	139	14700	41200
1	1	27	6782	-1012	1	4	235	51538	1167	2	-1	142	15000	42345
1	1	28	6292	4183	1	4	240	53070	-2034	2	-1	145	15300	43500
1	1	29	5772	-1344	1	4	245	54618	1364	2	-1	148	15600	44665
1	1	30	5222	6457	1	4	250	56182	-2223	2	-1	151	15900	45840
1	1	31	4642	-1012	1	4	255	57762	1167	2	-1	154	16200	47025
1	1	32	4032	4183	1	4	260	59358	-2034	2	-1	157	16500	48220
1	1	33	3392	-1344	1	4	265	60970	1364	2	-1	160	16800	49425
1	1	34	2722	6457	1	4	270	62598	-2223	2	-1	163	17100	50640
1	1	35	2032	-1012	1	4	275	64242	1167	2	-1	166	17400	51865
1	1	36	1322	4183	1	4	280	65902	-2034	2	-1	169	17700	53100
1	1	37	592	-1344	1	4	285	67578	1364	2	-1	172	18000	54345
1	1	38	-162	6457	1	4	290	69270	-2223	2	-1	175	18300	55600
1	1	39	-852	-1012	1	4	295	70978	1167	2	-1	178	18600	56865
1	1	40	-1682	4183	1	4	300	72702	-2034	2	-1	181	18900	58140
1	1	41	-2512	-1344	1	4	305	74442	1364	2	-1	184	19200	59425
1	1	42	-3342	6457	1	4	310	76198	-2223	2	-1	187	19500	60720
1	1	43	-4172	-1012	1	4	315	77970	1167	2	-1	190	19800	62025
1	1	44	-5002	4183	1	4	320	79758	-2034	2	-1	193	20100	63340
1	1	45	-5832	-1344	1	4	325	81562	1364	2	-1	196	20400	64665
1	1	46	-6662	6457	1	4	330	83382	-2223	2	-1	199	20700	66000
1	1	47	-7492	-1012	1	4	335	85218	1167	2	-1	202	21000	67345
1	1	48	-8322	4183	1	4	340	87070	-2034	2	-1	205	21300	68700
1	1	49	-9152	-1344	1	4	345	88938	1364	2	-1	208	21600	70065
1	1	50	-9982	6457	1	4	350	90822	-2223	2	-1	211	21900	71440
1	1	51	-10812	-1012	1	4	355	92722	1167	2	-1	214	22200	72825
1	1	52	-11642	4183	1	4	360	94638	-2034	2	-1	217	22500	74220
1	1	53	-12472	-1344	1	4	365	96570	1364	2	-1	220	22800	75625
1	1	54	-13302	6457	1	4	370	98518	-2223	2	-1	223	23100	77040
1	1	55	-14132	-1012	1	4	375	100482	1167	2	-1	226	23400	78465
1	1	56	-14962	4183	1	4	380	102462	-2034	2	-1	229	23700	79900
1	1	57	-15792	-1344	1	4	385	104458	1364	2	-1	232	24000	81345
1	1	58	-16622	6457	1	4	390	106470	-2223	2	-1	235	24300	82800
1	1	59	-17452	-1012	1	4	395	108498	1167	2	-1	238	24600	84265
1	1	60	-18282	4183	1	4	400	110542	-2034	2	-1	241	24900	85740
1	1	61	-19112	-1344	1	4	405	112602	1364	2	-1	244	25200	87225
1	1	62	-19942	6457	1	4	410	114678	-2223	2	-1	247	25500	88720
1	1	63	-20772	-1012	1	4	415	116770	1167	2	-1	250	25800	90225
1	1	64	-21602	4183	1	4	420	118878	-2034	2	-1	253	26100	91740
1	1	65	-22432	-1344	1	4	425	120992	1364	2	-1	256	26400	93265
1	1	66	-23262	6457	1	4	430	123122	-2223	2	-1	259	26700	94800
1	1	67	-24092	-1012	1	4	435	125268	1167	2	-1	262	27000	96345
1	1	68	-24922	4183	1	4	440	127430	-2034	2	-1	265	27300	97900
1	1	69	-25752	-1344	1	4	445	129608	1364	2	-1	268	27600	99465
1	1	70	-26582	6457	1	4	450	131802	-2223	2	-1	271	27900	101040
1	1	71	-27412	-1012	1	4	455	134012	1167	2	-1	274	28200	102625
1	1	72	-28242	4183	1	4	460	136238	-2034	2	-1	277	28500	104220
1	1	73	-29072	-1344	1	4	465	138480	1364	2	-1	280	28800	105825
1	1	74	-29902	6457	1	4	470	140738	-2223	2	-1	283	29100	107440
1	1	75	-30732	-1012	1	4	475	143012	1167	2	-1	286	29400	109065
1	1	76	-31562	4183	1	4	480	145302	-2034	2	-1	289	29700	110700
1	1	77	-32392	-1344	1	4	485	147608	1364	2	-1	292	30000	112345
1	1	78	-33222	6457	1	4	490	149930	-2223	2	-1	295	30300	114000
1	1	79	-34052	-1012	1	4	495	152268	1167	2	-1	29		

Table 2. *Heavy atom coordinates*

(a) Final coordinates of the heavy atoms with their estimated standard deviations (in parentheses)

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
I	0.4212 (3)	0.1266 (2)	0.4089 (1)
O(1)	0.0617 (44)	-0.2695 (20)	0.0065 (8)
O(2)	0.2538 (46)	-0.4489 (20)	0.0761 (9)
C(1)	0.7395 (41)	0.3159 (22)	0.2836 (8)
C(2)	0.6807 (38)	0.3308 (23)	0.3595 (10)
C(3)	0.7890 (54)	0.4829 (27)	0.4113 (11)
C(4)	0.9644 (45)	0.6239 (27)	0.3841 (12)
C(5)	1.0273 (48)	0.6140 (26)	0.3066 (13)
C(6)	0.9161 (48)	0.4622 (25)	0.2580 (11)
C(7)	0.6147 (39)	0.1575 (20)	0.2232 (9)
C(8)	0.4551 (49)	0.1800 (26)	0.1587 (11)
C(9)	0.3303 (48)	0.0314 (25)	0.1052 (10)
C(10)	0.3738 (45)	-0.1396 (27)	0.1156 (10)
C(11)	0.5559 (44)	-0.1554 (21)	0.1798 (9)
C(12)	0.6771 (47)	-0.0117 (26)	0.2336 (11)
C(13)	0.2219 (54)	-0.2970 (31)	0.0639 (8)

(b) Orthogonal coordinates for the heavy atoms coordinates with respect to the axes:

$$X' = X \sin \gamma + Z(\cos \beta - \cos \alpha \cos \gamma) / \sin \gamma$$

$$Y' = Y + X \cos \gamma + Z \cos \alpha$$

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

	<i>X'</i>	<i>Y'</i>	<i>Z'</i>
I	1.3966 Å	-0.4072 Å	7.1713 Å
O(1)	0.2485	-2.1357	0.1147
O(2)	0.9814	-3.8240	1.3339
C(1)	2.8088	1.2341	4.9744
C(2)	2.5047	1.1676	6.3049
C(3)	2.9077	2.1379	7.2138
C(4)	3.6515	3.2079	6.7358
C(5)	3.9738	3.3149	5.3780
C(6)	3.5565	2.3404	4.5244
C(7)	2.3453	0.2490	3.9153
C(8)	1.7419	0.6926	2.7827
C(9)	1.2721	-0.2361	1.8451
C(10)	1.4427	-1.6114	2.0275
C(11)	2.1390	-2.0146	3.1526
C(12)	2.5933	-1.1221	4.0961
C(13)	0.8605	-2.5981	1.1199

than 3.6 Å are shown in Table 5; the bond lengths and angles together with some of the intramolecular non-bonded distances are in Table 6. The equations of the ring system C(1)-C(6), C(7)-C(12), and the group C(10), 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 a plane perpendicular to *b'*, and *c'* is perpendicular to *a'* and *b'*, together with the deviations of the atoms from the planes are given in Table 7. The angle between the phenyl rings is 51.3° and the angle between the carboxyl group and the phenyl ring C(7)-C(12) is 5.2°.

Table 4. *Hydrogen atom parameters*

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

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
H(1)	-0.049	-0.375	-0.025
H(3)	0.742	0.481	0.474
H(4)	1.047	0.736	0.427
H(5)	1.155	0.733	0.289
H(6)	0.951	0.460	0.201
H(8)	0.392	0.312	0.150
H(9)	0.179	0.045	0.054
H(11)	0.620	-0.287	0.187
H(12)	0.827	-0.028	0.283

Table 5. *Intermolecular distances between atoms less than 3.6 Å apart (excluding hydrogen atoms)*

<i>i</i>	<i>j</i>	Equi-point indication	<i>d_{ij}</i> Å
O(1)	C(9)	\bar{x} \bar{y} \bar{z}	3.432 Å
O(2)	O(2)	1 - <i>x</i> 1 - <i>y</i> \bar{z}	3.485
C(3)	C(3)	\bar{x} 1 - <i>y</i> 1 - <i>z</i>	3.533
O(1)	O(1)	\bar{x} 1 - <i>y</i> \bar{z}	3.502
O(1)	O(2)	\bar{x} 1 - <i>y</i> \bar{z}	2.597
O(1)	C(13)	\bar{x} 1 - <i>y</i> \bar{z}	3.425
O(2)	C(13)	\bar{x} 1 - <i>y</i> \bar{z}	3.335
O(2)	O(2)	\bar{x} 1 - <i>y</i> \bar{z}	3.313

Table 3. *Thermal parameters in Å² for the heavy atoms*

	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>2U₂₃</i>	<i>2U₃₁</i>	<i>2U₁₂</i>
I	0.044 (1)	0.038 (1)	0.036 (1)	0.018 (1)	0.009 (1)	-0.009 (1)
O(1)	0.110 (13)	0.039 (8)	0.040 (7)	0.014 (13)	-0.059 (16)	-0.003 (17)
O(2)	0.106 (13)	0.038 (8)	0.050 (8)	-0.003 (14)	-0.035 (17)	-0.009 (17)
C(1)	0.038 (10)	0.034 (9)	0.024 (7)	0.032 (14)	-0.014 (13)	0.010 (15)
C(2)	0.017 (8)	0.030 (8)	0.050 (10)	0.026 (16)	-0.007 (13)	0.020 (13)
C(3)	0.061 (13)	0.042 (11)	0.042 (10)	-0.014 (17)	-0.017 (18)	-0.037 (19)
C(4)	0.036 (11)	0.048 (12)	0.052 (10)	0.029 (19)	-0.016 (16)	-0.002 (19)
C(5)	0.041 (12)	0.033 (10)	0.070 (13)	0.017 (19)	0.011 (19)	0.005 (17)
C(6)	0.049 (12)	0.032 (9)	0.045 (10)	0.007 (16)	0.016 (17)	0.030 (17)
C(7)	0.029 (9)	0.021 (7)	0.038 (8)	0.030 (13)	-0.007 (13)	0.012 (13)
C(8)	0.049 (12)	0.039 (10)	0.044 (10)	0.032 (17)	-0.006 (17)	0.045 (18)
C(9)	0.053 (12)	0.034 (9)	0.042 (9)	0.016 (16)	0.003 (17)	0.028 (18)
C(10)	0.037 (11)	0.049 (11)	0.041 (9)	0.025 (18)	-0.008 (15)	0.043 (18)
C(11)	0.048 (11)	0.022 (8)	0.028 (7)	0.018 (13)	-0.025 (14)	0.001 (15)
C(12)	0.045 (11)	0.040 (10)	0.048 (10)	0.042 (18)	-0.001 (17)	0.031 (18)
C(13)	0.072 (13)	0.065 (13)	0.009 (6)	0.009 (15)	-0.001 (15)	0.024 (22)

Table 6. Bond lengths and angles with their e.s.d.'s

	Length	E.s.d.		Length	E.s.d.
I—C(2)	2.112 Å	0.017 Å	C(2)—C(3)	1.389 Å	0.027 Å
I—C(7)	3.454	0.016	C(3)—C(4)	1.388	0.029
I—C(12)	3.376	0.020	C(4)—C(5)	1.400	0.029
O(1)—C(9)	2.766	0.025	C(5)—C(6)	1.361	0.029
O(1)—C(10)	2.315	0.025	C(7)—C(8)	1.358	0.025
O(1)—C(13)	1.264	0.026	C(7)—C(12)	1.405	0.025
O(2)—C(10)	2.364	0.026	C(8)—C(9)	1.401	0.027
O(2)—C(11)	2.815	0.024	C(9)—C(10)	1.398	0.027
O(2)—C(13)	1.250	0.026	C(10)—C(11)	1.383	0.026
C(1)—C(2)	1.366	0.024	C(10)—C(13)	1.462	0.028
C(1)—C(6)	1.409	0.025	C(11)—C(12)	1.376	0.026
C(1)—C(7)	1.519	0.023			
	Angle	E.s.d.		Angle	E.s.d.
I—C(2)—C(1)	123.6°	1.3°	C(2)—C(3)—C(4)	118.0°	1.8°
I—C(2)—C(3)	113.9	1.3	C(3)—C(4)—C(5)	121.1	1.9
O(1)—C(13)—O(2)	122.8	2.0	C(4)—C(5)—C(6)	118.9	1.9
O(1)—C(13)—C(10)	116.1	1.8	C(8)—C(7)—C(12)	120.3	1.6
C(2)—C(1)—C(7)	125.4	1.5	C(8)—C(9)—C(10)	121.6	1.8
C(1)—C(2)—C(3)	122.6	1.7	C(9)—C(10)—C(11)	117.0	1.7
C(6)—C(1)—C(7)	116.6	1.5	C(9)—C(10)—C(13)	122.3	1.8
C(1)—C(6)—C(5)	121.6	1.8	C(11)—C(10)—C(13)	120.6	1.7
C(1)—C(7)—C(8)	120.4	1.5	C(10)—C(11)—C(12)	122.3	1.7
C(1)—C(7)—C(12)	119.3	1.5	O(2)—C(13)—C(10)	121.1	1.9
C(2)—C(1)—C(6)	117.9	1.6			

Table 7. Equations of the mean planes of the ring systems

I, C(1)—C(6); II, C(7)—C(12); III, C(10), C(13), O(1) and O(2).

$$\text{I } 0.8455X' - 0.5077Y' + 0.1653Z' = 2.5678$$

$$\text{II } 0.8723X' + 0.0642Y' - 0.4848Z' = 0.1939$$

$$\text{III } 0.8496X' - 0.0120Y' - 0.5273Z' = 0.1751$$

Deviations from the mean planes

	I	II	III
I	0.005 Å		
C(1)	0.003	-0.076 Å	-0.426 Å
C(2)	-0.001		
C(3)	-0.003		
C(4)	0.004	-0.068	-0.663
C(5)	-0.002		
C(6)	-0.001		
C(7)	-0.064	-0.030	-0.250
C(8)		0.021	-0.171
C(9)		0.006	-0.064
C(10)	-0.195	-0.022	0.001
C(11)		0.014	0.004
C(12)		0.010	-0.118
C(13)	-0.336	-0.153	-0.003
O(1)		-0.170	0.001
O(2)		-0.230	0.001

Discussion

The angle of $51.3 \pm 1.2^\circ$ between the two phenyl rings is smaller than had been expected if a simple treatment of setting the I to H(12) distance equal to the sum of their respective van der Waals radii is used. A similar discrepancy has been observed in the case of 2'-chlorobiphenyl-4-carboxylic acid (Sutherland, 1969), 4-acetyl-2'-chlorobiphenyl (Sutherland & Hoy, 1968), and 2-chlorobiphenyl-4-carboxylic acid (Sutherland & Hoy, 1969).

In common with these structures not only is there a rotation of one ring with respect to the other by an angle φ_1 about C(1)—C(7) but also two other rotations, which are a rotation φ_2 of the ring C(1)—C(6) about an axis which is in the plane of that ring and passes through C(1) perpendicular to C(1)—C(7) and a rotation φ_3 of ring C(7)—C(12) about an axis which is in the plane of that ring and passes through C(7) perpendicular to C(1)—C(7), the notation used being that of Chawdhury, Hargreaves & Sullivan (1968).

In the present structure the angles φ_2 and φ_3 are respectively 2.5 ± 0.7 and $1.7 \pm 0.7^\circ$. The angle φ_2 is somewhat larger than the values of 0.4 and 0.5° in 2'-chlorobiphenyl-4-carboxylic acid and 4-acetyl-2'-chlorobiphenyl respectively. In the case of 2'-chlorobiphenyl-4-carboxylic acid the Cl—C(2) bond was displaced out of the plane of the biphenyl ring C(1)—C(6) by 1.8° . No significant displacement was observed in the case of the I—C(2) bond and this may account for the increased value of φ_2 . The I—C(2) bond length of 2.122 ± 0.017 Å is possibly significantly longer than the value of 2.05 ± 0.01 Å quoted in *International Tables for X-ray Crystallography* (1962).

The C(1)—C(7) bond length of 1.519 ± 0.023 Å is similar to that of 1.502 ± 0.010 Å for 2'-chlorobiphenyl-4-carboxylic acid and 1.506 ± 0.017 Å for biphenyl (Hargreaves & Rizvi, 1962) and is not significantly different from the biphenyl bond lengths of 1.487 ± 0.010 Å in 2-chlorobiphenyl-4-carboxylic acid, 1.490 ± 0.010 Å in 4-acetyl-2'-chlorobiphenyl and 1.479 ± 0.010 Å in 4-acetyl-2'-fluorobiphenyl.

The exocyclic C(10)—C(13) bond was found to be 1.462 ± 0.028 Å. Neither the C(1)—C(7) bond nor the C(10)—C(13) bond differ significantly from the theoret-

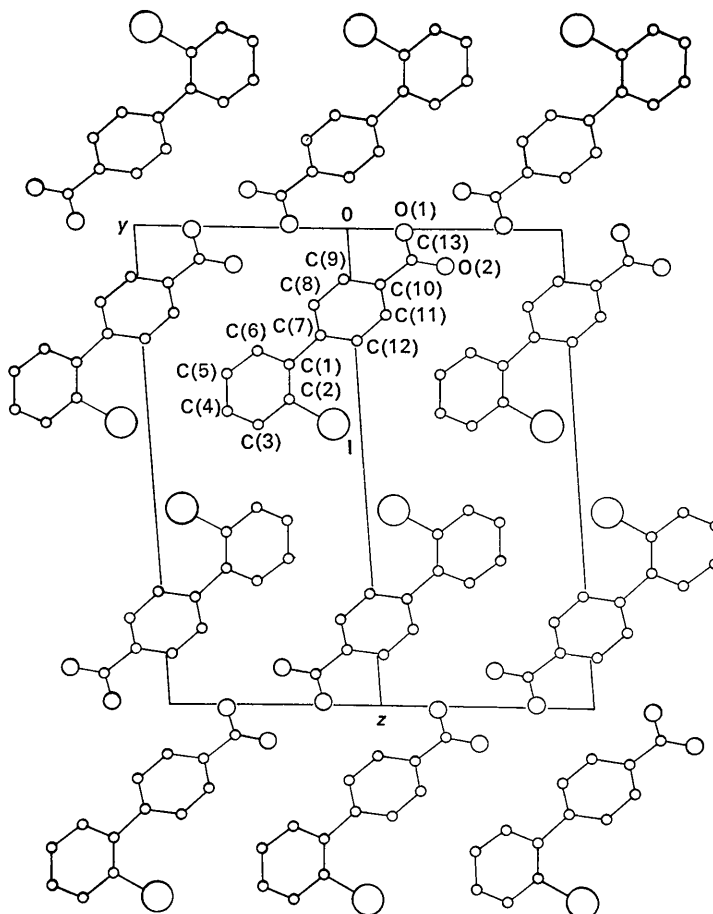


Fig. 1. The arrangement of the molecules in the unit-cell viewed along the *a* axis.

ical value of 1.477 \AA quoted by Dewar & Schmeising (1959) and Cruickshank & Sparks (1960) for the (*sp*²) single-bond length between trigonally linked carbon atoms.

The carboxyl group is rotated about the C(10)–C(13) bond through an angle φ_4 of $5.2 \pm 1.3^\circ$. Associated with this is a second rotation φ_5 of the group C(10), C(13), O(1) and O(2) about an axis which is in the plane of that group and passes through C(10) perpendicular to C(7)–C(10). The angle of φ_5 was found to be $4.8 \pm 0.8^\circ$. These are comparable with the angles of 5.6 and 7.1° for φ_4 and φ_5 respectively obtained for 2'-chlorobiphenyl-4-carboxylic acid.

In the solid phase biphenyl is planar. The introduction of an iodine atom in the 2' position causes a strain which results in a twisting of the rings about the biphenyl bond, φ_1 , together with the additional small rotations of φ_2 and φ_3 . It is probable that there is a relayed steric effect which results in the rotation and displacement of the carboxyl group. Similar effects have been observed in other 2, 2' and 3' halogen derivatives of biphenyl investigated by the author.

The C(13)–O(1) bond of $1.264 \pm 0.026 \text{ \AA}$ and the C(13)–O(2) bond of $1.250 \pm 0.026 \text{ \AA}$ were respectively

shorter and longer than had been expected. The bond lengths are similar to those obtained in 2'-chlorobiphenyl-4-carboxylic acid of 1.289 ± 0.010 and $1.261 \pm 0.010 \text{ \AA}$ respectively.

The O–H...O bond of 2.60 \AA , which is the shortest intermolecular distance, is similar to the values quoted for 2-chlorobiphenyl-4-carboxylic acid of 2.62 \AA and orthochlorobenzoic acid of 2.63 \AA (Ferguson & Sim, 1961). The bond angles C(10)–C(13)–O(1), C(10)–C(13)–O(2) and O(1)–C(13)–O(2) are comparable with those found in similar compounds.

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Crystallography of the Silver-Rich Rare-Earth-Silver Intermetallic Compounds

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The crystal structures of the silver-rich compounds in the rare-earth-silver systems were determined by means of X-ray powder diffraction methods. Metallographic methods were used to confirm the stoichiometries. The low temperature form of LaAg_5 crystallizes in a 'substituted' MgZn_2 ($C14$) type Laves-phase structure. The high temperature polymorph of LaAg_5 and the phases CeAg_5 , PrAg_5 and YbAg_5 were found to be isotypic but the crystal structure was not established. EuAg_5 crystallizes in the CaCu_5 ($D2_a$) type structure; LuAg_4 and ScAg_4 of the MoNi_4 ($D1_a$) type were found. $R_{14}\text{Ag}_{51}$ phases of the $\text{Gd}_{14}\text{Ag}_{51}$ type exist for $R = \text{Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho}$ and Er . Yb_2Ag_7 crystallizes in the Ca_2Ag_7 type structure. TmAg_3 was found to exist in both the AuCu_3 ($L1_2$) type and the TiCu_3 ($D0_a$) type structures. The crystallographic data for these phases are given and their structural relationships are discussed.

Introduction

During an investigation of the solubility limits of the rare earths in silver, it became necessary to determine the stoichiometry of the first silver-rich compound in the rare-earth-silver systems (Gschneidner, McMasters, Alexander & Venteicher, 1970). Since most of these compounds are new, their structural properties and crystallographic data were determined and are the subject of this paper.

All of the rare earths except europium form the RAg compound with the cubic CsCl ($B2$) type structure. These phases have been studied by several investigators and most of their results are given in Pearson (1967) and McMasters & Gschneidner (1964). For YbAg and YAg the data are given by Moriarty, Humphreys, Gordon & Baenziger (1966). Iandelli & Palenzona (1969) have shown that YbAg crystallizes in both the CsCl and FeB type structures. Köster & Meixner (1965) reported that EuAg exists but the structure was not established.

For $R = \text{La, Ce, Pr, Nd, Eu}$ and Yb the phase RAg_2 crystallizes in the orthorhombic CeCu_2 (KHg_2) type structure according to Iandelli & Palenzona (1968) and Köster & Meixner (1965) in the case of EuAg_2 . For $R = \text{Gd, Tb, Dy, Ho, Er, Tm, Lu, Sc}$ and Y the

RAg_2 phase of the tetragonal MoSi_2 ($C11_b$) type structure has been reported by several investigators: Baenziger & Moriarty (1961), Moriarty, Gordon & Humphreys (1965), Dwight, Downey & Conner (1967), Kusma & Laube (1965), Ferro, Capelli, Borsese & Delfino (1967), Iandelli & Palenzona (1968), and Steeb, Godel & Lohr (1968). Different structures have been reported for SmAg_2 by Iandelli & Palenzona (1968), for YbAg_2 by Moriarty, Humphreys, Gordon & Baenziger (1966), and for YAg_2 by Gebhardt, von Erdberg & Lütz (1964).

The structure data for the RAg_3 phases reported by Steeb, Godel & Lohr (1968) and Donalato & Steeb (1969) will be discussed later in connection with the results of our investigation.

Lattice parameters and structure types for Yb_5Ag_3 (Cr_5B_3 type) and Yb_3Ag_2 (U_3Si_2 type) were determined by Iandelli & Palenzona (1969). Palenzona (1967) and Köster & Meixner (1965) reported EuAg_5 as being of the hexagonal CaCu_5 ($D2_a$) type structure. The latter also reported that the phases EuAg_4 and Eu_5Ag_3 exist but did not determine the structures.

Experimental procedures

The purity of the metals used in this investigation and alloy preparation procedures are described by Gschnei-