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The Molecular Structure of 3,3′-Spirobi-(3-selenaphthalide)

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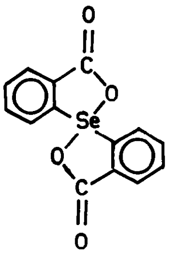
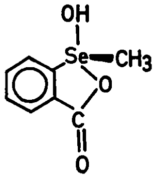
Crystals of 3,3′-spirobi-(3-selenaphthalide) are monoclinic, $C2/c$, with cell constants $a=13{\cdot}646$ (2), $b=8{\cdot}639$ (3), $c=10{\cdot}034$ (2) Å and $\beta=96{\cdot}64$ (2)°. The identical halves of the molecule are related by a twofold axis. The configuration around the selenium atom is a trigonal bipyramid with the selenium-bonded oxygen atoms at the apical positions. The benzene-ring planes form a dihedral angle of 102·7°.

Introduction

3,3′-Spirobi-(3-selenaphthalide), (I), (SSP), was first synthesized by Lesser & Weiss (1914). The synthesis has now been re-examined by Dr Björn Lindgren (Dahlén & Lindgren, 1973) of Uppsala University. An X-ray single-crystal analysis was performed to verify the proposed chemical structure. This would also allow a comparison with *o*-carboxyphenyl methyl selenoxide, (II), (OCSeO) (Dahlén, 1973), which according to the proposed structural formula would have features similar to SSP.



(I)



(II)

Experimental

Crystal data

3,3′-Spirobi-(3-selenaphthalide)

Molecular formula	$(C_7H_4O_2)_2Se$
Unit cell	monoclinic $a=13{\cdot}646$ (2), $b=8{\cdot}639$ (3), $c=10{\cdot}034$ (2) Å, $\beta=96{\cdot}64$ (2)°
V	1175 Å^3
Molecular weight	319·18
Z	4
D_c	1·804 g cm^{-3}
D_m	1·803 g cm^{-3}
Space group	$C2/c$
Systematically absent reflexions	hkl: $h+k=2n+1$; $h0l$: $l=2n+1$
Crystal dimensions	0·30 × 0·18 × 0·30 mm
λ	1·54051 Å (Cu $K\alpha_1$ radiation)
μ	49·35 cm^{-1} for Cu $K\alpha$ radiation.

A single crystal was mounted with the b axis coinciding with the φ axis of the diffractometer. Data were recorded on a Picker FACS I automatic diffractometer using the Vanderbilt disc-oriented diffractometer system, by Dr P. G. Lenhert. Graphite-monochromated Cu $K\alpha$ radiation was used to measure intensities up to $2\theta=124°$. The θ–2θ mode was used, scanning the reflexions in 8 steps of 2 s with a step size of 0·3°. Stationary background counts were taken at both sides of the peaks. In all, 913 reflexions were recorded. 891 of these were more than 2σ above background and were considered observed. Only these observed reflexions were used in the structure refinement. Data were corrected for Lorentz and polarization effects and for absorption. Scattering factors for carbon, oxygen and selenium atoms were those in *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms those of Stewart, Davidson & Simpson (1965). The scattering factors for selenium and oxygen were corrected for the real component of anomalous dispersion ($\Delta f'=-0{\cdot}879$ and 0·047 respectively) (Cromer & Liberman, 1970). Calculations were performed on a Datasaab D21–PDP 15 dual computer system using programs developed at this institute. The absorption correction, however, was performed on an IBM 360/65 computer using the program *DATAP*2, in use at the Department of Inorganic Chemistry of Göteborg, originally written by Coppens, Leiserowitz & Rabinovich (1965).

Structure determination and refinement

From the systematically absent reflexions the space group could be either Cc or $C2/c$. From the symmetrical form of the molecule the space group was assumed to be $C2/c$ with the selenium atom located on the twofold axis. From a sharpened Patterson synthesis the y coordinate of the selenium atom was easily obtained. The selenium-phased Fourier synthesis then revealed all the other non-hydrogen atoms. A structure-factor calculation with these 10 atoms included gave an R value of 0·20. Block-diagonal refinement varying all positional parameters and isotropic temperature factors lowered R to 0·10. A Fourier difference map was then calculated from which the hydrogen atoms were located. The structure was refined with full-matrix methods refining all positional parameters, anisotropic temperature factors for the heavier atoms and isotropic for the hydrogen atoms. The refinement was terminated when the average value of shift per standard deviation was 0·16. The R value was then 0·043. The weight assigned to each observation in the refinement was (Mills & Rollett, 1961):

$$w = 1 + [(|F_o| - 3{\cdot}2\ |F_{\min}|)/6{\cdot}4\ |F_{\min}|]^2.$$

Results and discussion

The final atomic coordinates are given in Table 1. Table 2 gives the observed and calculated structure factors. The interatomic bond distances and angles are

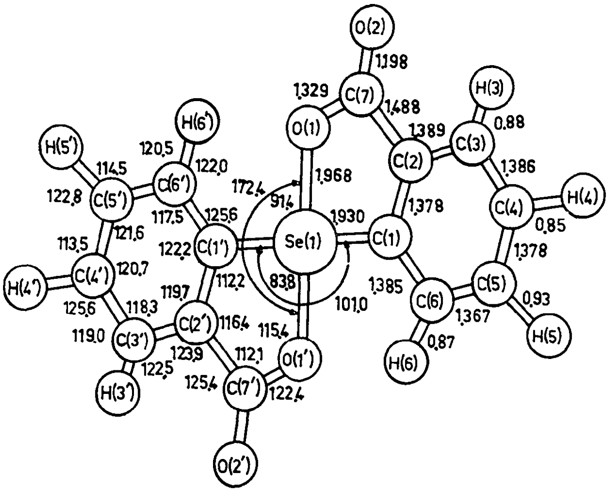


Fig. 1. Bond lengths and angles.

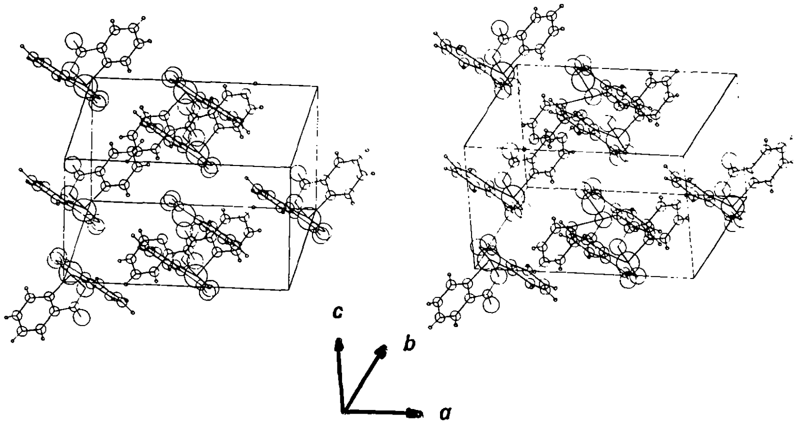


Fig. 2. Stereoscopic pair of 3,3′-spirobi-(3-selenaphthalide) viewed along the c axis.

Table 1. *Fractional atomic coordinates and thermal parameters with standard deviations*

All values except B have been multiplied by 10^4. The anisotropic temperature factors are in the form

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

(*a*) Heavier atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Se(1)	0 (-)	902 (11)	2500 (-)	296 (9)	366 (10)	518 (10)	0 (—)	86 (10)	0 (—)
C(1)	−820 (5)	2323 (9)	1642 (7)	235 (34)	415 (40)	395 (37)	−49 (30)	−70 (28)	3 (29)
C(2)	428 (6)	2677 (10)	351 (8)	295 (38)	501 (45)	372 (38)	−91 (33)	18 (30)	50 (32)
C(3)	937 (7)	3660 (13)	−421 (9)	489 (52)	618 (53)	397 (45)	55 (44)	49 (38)	50 (46)
C(4)	1824 (8)	4280 (12)	152 (11)	462 (57)	587 (58)	587 (60)	91 (42)	117 (45)	−68 (41)
C(5)	2210 (7)	3877 (11)	1435 (10)	349 (47)	529 (49)	554 (54)	−28 (41)	18 (39)	−134 (38)
C(6)	1723 (6)	2896 (10)	2201 (8)	283 (39)	539 (47)	379 (41)	−21 (34)	−13 (31)	−21 (34)
C(7)	−531 (6)	1935 (11)	−137 (8)	298 (39)	627 (54)	453 (47)	−208 (39)	2 (35)	24 (36)
O(1)	−867 (5)	1053 (8)	795 (7)	317 (35)	687 (46)	619 (42)	−240 (31)	52 (29)	−163 (27)
O(2)	−964 (5)	2079 (10)	−1239 (7)	486 (39)	1160 (64)	478 (38)	−262 (38)	−120 (31)	41 (38)

(*b*) Hydrogen atoms

	x	y	z	B (Å^2)
H(3)	740 (86)	3850 (125)	−1267 (112)	5·6 (2·3)
H(4)	2206 (63)	4854 (108)	−248 (86)	9·3 (1·7)
H(5)	2744 (86)	4390 (118)	1901 (109)	5·6 (2·4)
H(6)	1987 (60)	2629 (101)	3003 (87)	3·5 (1·7)

Table 2. *Observed and calculated structure factors* (× 100)

H	K	L	FOBS	FCALC
0	0	2	612	436
0	0	4	4410	9101
0	0	6	3570	3703
0	0	8	5310	5248
0	0	10	4185	3168
0	2	0	7212	6474
0	2	1	7552	7478
0	2	2	2979	2898
0	2	3	5189	5301
0	2	4	3585	3427
0	2	5	17079	9401
0	2	6	4553	4099
0	2	7	3075	3690
0	2	8	1160	1001
0	2	9	1241	1173
0	2	11	2270	2477
0	4	0	4053	5794
0	4	1	9094	6892
0	4	2	2134	1942
0	4	3	4430	4239
0	4	4	3345	3252
0	4	5	5521	5204
0	4	6	4625	4504
0	4	7	4530	4305
0	4	8	1674	1711
0	4	9	1960	1905
0	4	10	1011	1040
0	6	0	8560	9294
0	6	1	3168	2966
0	6	2	5128	5023
0	6	3	332	331
0	6	4	3948	3702
0	6	5	4445	4105
0	6	6	2791	2741
0	6	8	2142	2117
0	6	9	1020	1008
0	8	1	3371	3248
0	8	2	543	504
0	8	3	3307	3217
0	8	4	1514	1472
0	8	5	1925	1802
0	8	6	303	329
1	9	-4	280	314
1	9	-3	2625	2629
1	9	-2	1051	1509
1	9	-1	2082	2825
1	9	0	1342	1318
1	9	1	2479	2394
1	9	2	943	918
1	9	3	2464	2400
1	9	4	275	216
1	7	-8	1517	1597
1	7	-7	2580	2419
1	7	-6	2712	2600
1	7	-5	2376	2301
1	7	-4	1110	1135
1	7	-3	1510	1402
1	7	-2	3079	2950
1	7	-1	4080	3810
1	7	0	3752	4040
1	7	1	5426	5193
1	7	2	3085	3065
1	7	3	2412	2248
1	7	4	1902	1827
1	7	5	3038	2855
1	7	6	608	827
1	7	7	524	497
1	5	-9	1009	1016
1	5	-8	833	947
1	5	-7	324	201
1	5	-6	4700	4403
1	5	-5	1319	1301
1	5	-4	5125	5010
1	5	-3	1700	1723
1	5	-2	10164	9603
1	5	-1	2737	2583
1	5	0	4858	5506
1	5	1	4576	4403
1	5	2	4136	4102
1	5	3	235	145
1	5	4	6246	6039
1	5	5	3291	3193
1	5	6	7510	7239
1	5	8	2310	2224
1	5	9	1347	1340
1	3	-10	445	408
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1	3	-8	2035	1998
1	3	-7	9660	9027
1	3	-6	726	569
1	3	-5	5557	5213
1	3	-4	887	631
1	3	-3	6565	6706
1	3	-2	746	527
1	3	-1	6389	6089
1	3	0	3984	4004
1	3	1	11680	12107
1	3	2	282	145
1	3	3	4541	4475
1	3	4	1728	1573
1	3	5	6152	5971
1	3	7	3966	3900
1	3	8	542	811
1	3	9	2435	2369
1	1	-11	1063	1068
1	1	-10	1547	1504
1	1	-9	1597	1512
1	1	-8	3612	3348
1	1	-7	1208	1096
1	1	-6	7135	6708
1	1	-5	1722	1727
1	1	-4	5550	5009
1	1	-3	6173	5708
1	1	-2	13713	13315
1	1	-1	8279	7277
1	1	0	9082	11651
1	1	1	11576	12414
1	1	2	6017	5855
1	1	3	8067	7849
1	1	4	4271	4263
1	1	5	9551	8751
1	1	6	7118	6367
1	1	7	1303	1305
1	1	8	3298	3712
1	1	9	380	379
1	1	10	1326	1210
1	1	11	2208	2366
2	0	-10	1014	1047
2	0	-8	5296	4893
2	0	-6	8962	7904
2	0	-4	2944	2715
2	0	-2	2235	1909
2	0	2	8286	8465
2	0	4	14418	15615
2	0	6	4637	4537
2	0	8	2324	1991
2	0	10	4349	4744
2	2	-11	2166	2309
2	2	-10	1174	1158
2	2	-9	3556	3473
2	2	-8	688	811
2	2	-7	4643	4372
2	2	-6	5465	4408
2	2	-5	8181	5998
2	2	-4	4542	3797
2	2	-3	3670	3603
2	2	-2	17527	17717
2	2	0	1380	3354
2	2	1	1917	2915
2	2	2	2441	2561
2	2	3	4450	6510
2	2	4	1260	1362
2	2	5	6487	6378
2	2	6	5450	5134
2	2	7	5482	5532
2	2	8	1180	1144
2	2	9	2081	1963
2	2	10	410	426
2	4	-10	784	790
2	4	-9	1959	1966
2	4	-8	575	641
2	4	-7	2549	2519
2	4	-6	7306	6845
2	4	-5	4475	4354
2	4	-4	3471	3356
2	4	-3	2756	2675
2	4	-2	10786	10744
2	4	-1	6182	6135
2	4	0	2651	3140
2	4	1	6952	7325
2	4	2	234	266
2	4	3	3012	3051
2	4	4	6644	6703
2	4	5	4657	4679
2	4	6	3382	3235
2	4	7	2682	2603
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2	8	3	3835	3597
2	8	4	858	708
2	8	5	2053	2038
2	8	6	816	859
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3	3	0	2683	2938
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3	3	2	6100	6822
3	3	3	3770	6870
3	3	4	2585	2530
3	3	5	6118	6151
3	3	6	341	390
3	3	7	4372	4959
3	3	8	341	310
3	3	9	2561	2524
3	3	10	911	877
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3	1	-10	972	1928
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5	7	-7	2127	2191
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5	7	-5	1597	1599
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5	7	-3	3286	3352
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5	7	0	305	410
5	7	1	3671	3766
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5	7	3	2937	2865
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5	5	1	1097	1701
5	5	2	4631	4940
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5	5	4	3605	4019
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5	5	7	685	949
5	5	8	1698	1958
5	3	-9	2799	2956
5	3	-8	512	379
5	3	-7	2214	2193
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5	3	-1	8271	9002
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5	3	2	612	305
5	3	3	8714	9034
5	3	4	3598	3334
5	3	5	4017	4097
5	3	6	850	829
5	3	7	1489	1510
5	3	8	645	113
5	3	9	3312	3502
5	1	-11	602	848
5	1	-10	2050	2103
5	1	-9	5184	5098
5	1	-8	2740	2838
5	1	-7	3655	3673
5	1	-6	3881	3811
5	1	-5	5487	4901
5	1	-4	8197	7894
5	1	-3	1957	2059
5	1	-2	10881	10819
5	1	-1	7557	6533
5	1	0	1274	1550
5	1	1	7749	8101
5	1	2	7133	7414
5	1	3	4136	4358
5	1	4	7182	7211
5	1	5	2389	2329
5	1	6	4525	4558
5	1	7	1902	1945
5	1	8	1782	1717
5	1	9	1209	1124
5	1	10	2141	2239
6	0	-8	6063	6501
6	0	-6	3291	3178
6	0	-4	15987	15501
6	0	-2	10053	9919
6	0	0	927	744
6	0	2	12149	13404
6	0	4	9217	9855
6	0	6	7010	6992
6	0	8	1245	1001
6	0	10	1372	1612
6	2	-10	1786	1988
6	2	-9	3480	3402
6	2	-8	1276	1265
6	2	-7	3364	3401
6	2	-6	1419	1759
6	2	-5	3626	3791
6	2	-4	522	221
6	2	-3	9353	8348
6	2	-2	1351	1502
6	2	-1	7009	7657
6	2	0	8229	6662
6	2	1	3234	3691
6	2	2	1240	1509
6	2	3	7684	8234
6	2	4	1986	1952
6	2	5	340	711
6	2	6	2912	2449
6	2	7	5250	5261
6	2	8	2500	2531
6	2	9	1854	1999
6	4	-9	1367	1374
6	4	-8	2385	2373
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6	4	-6	1985	2015
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6	4	-1	4929	5269
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6		2	5914	5771
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6	4	4	2799	2905
6	4	5	4311	4441
6	4	6	785	721
6	4	8	2156	2123
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6	6	-6	2451	2684
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6	6	-4	6114	6009
6	6	-3	4901	4909
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6	6	-1	627	813
6	6	0	3953	4807
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6	6	2	3310	3904
6	6	3	1160	1075
6	6	4	4290	4393
6	6	5	921	809
6	6	6	2629	2627
6	6	7	771	837
6	8	-6	2716	2095
6	8	-4	284	503
6	8	-3	2271	2761
6	8	-2	852	902
6	8	-1	3160	3118
6	8	0	1954	2817
6	8	1	1475	1335
6	8	2	445	275
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7	7	3	2186	2124
7	7	4	1895	1700
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7	5	-8	2286	2529
7	5	-7	1776	1926
7	5	-6	2126	2114
7	5	-5	344	207
7	5	-4	3719	3794
7	5	-3	3265	3324
7	5	-2	3597	3579
7	5	-1	792	701
7	5	0	6419	6700
7	5	1	2629	2857
7	5	2	6726	6907
7	5	3	260	378
7	5	4	3780	3919
7	5	5	1539	1794
7	5	6	920	948
7	5	7	766	808
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7	3	-6	983	1021
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7	3	0	376	304
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7	3	6	279	262
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7	3	8	330	298
7	3	9	1319	1469
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7	1	6	1681	1603
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7	1	8	7834	2849
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8	0	-8	2390	2405
8	0	-6	1558	1600
8	0	-4	8173	8700
8	0	-2	10439	10401
8	0	0	538	667
8	0	2	7521	7709
8	0	4	1337	1709
8	0	6	8999	9115
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8	2	5	2180	2200
8	2	6	1517	1499
8	2	7	2171	2100
8	2	8	651	777
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8	4	-3	3627	3708
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8	4	3	3176	3373
8	4	4	1985	2034
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8	4	6	1241	1263
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8	6	-4	4513	4742
8	6	-3	1376	1325
8	6	-2	4627	4479
8	6	-1	1082	1601
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8	6	2	3677	3711
8	6	3	555	676
8	6	4	1980	1905
8	6	5	696	635
8	6	6	2316	2401
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8	8	-3	2592	2403
8	8	-2	639	829
8	8	-1	3036	2985
8	8	1	2526	2546
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9	7	-5	1634	1631
9	7	-4	2792	2845
9	7	-3	2772	2772
9	7	-2	2395	2350
9	7	-1	2546	2438
9	7	0	3244	3109
9	7	1	3032	3018
9	7	2	1615	1919
9	7	3	1215	1200
9	5	-8	2118	2305
9	5	-7	542	664
9	5	-6	2794	2944
9	5	-5	1306	1301
9	5	-4	4943	5056
9	5	-3	2490	2501
9	5	-2	1306	1208
9	5	-1	617	524
9	5	0	2986	2936
9	5	1	549	535
9	5	2	4150	4190
9	5	3	610	574
9	5	4	3135	3243
9	5	5	572	501
9	5	6	1317	1399
9	3	-9	2612	2977
9	3	-8	627	711
9	3	-7	2962	2978
9	3	-6	1607	1719
9	3	-5	4526	4474
9	3	-3	3259	3231
9	3	-2	2926	3910
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9	3	0	750	507
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9	3	2	957	945
9	3	3	5594	5904
9	3	5	2072	2101
9	3	6	1683	1701
9	3	7	3380	3512
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9	1	-9	640	647
9	1	-8	2005	2118
9	1	-7	1470	1530
9	1	-6	4135	4207
9	1	-5	3562	3652
9	1	-4	6312	6375
9	1	-3	3634	3635
9	1	-2	4874	4728
9	1	-1	1114	1151
9	1	0	5296	5363
9	1	1	2546	2605
9	1	2	5605	5647
9	1	3	2330	2306
9	1	4	3387	3517
9	1	5	656	693
9	1	6	3343	3333
9	1	7	1441	1497
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10	0	-6	5500	5069
10	0	-4	5044	5017
10	0	-2	5909	5690
10	0	0	9015	8531
10	0	2	6177	6194
10	0	4	908	911
10	0	6	3006	3008
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10	2	-6	1724	1762
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10	2	-4	2970	2608
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10	2	-1	3793	3870
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10	2	2	1671	1708
10	2	3	1655	1710
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10	2	5	4659	4605
10	2	6	648	607
10	2	7	2037	2102
10	4	-8	1169	1327
10	4	-7	3512	3828
10	4	-6	2029	2981
10	4	-5	2232	2201
10	4	-4	3052	2971
10	4	-3	3683	3910
10	4	-2	1321	1338
10	4	-1	2977	2697
10	4	0	4070	4708
10	4	1	3949	4077
10	4	2	2866	2853
10	4	3	2074	2099
10	4	4	3571	3631
10	4	5	1313	1095
10	4	6	1621	1818
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10	6	-5	1094	1141
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10	6	-3	681	623
10	6	-2	3374	3313
10	6	-1	1095	1056
10	6	0	3947	3924
10	6	1	1090	909
10	6	2	3133	3221
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10	6	4	1565	1497
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11	5	-3	1692	1518
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11	5	0	3978	4055
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11	5	4	1954	1950
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11	3	-6	250	301
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11	3	-4	1221	1207
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11	3	4	1265	1169
11	3	5	3473	3407
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11	1	-7	1990	2017
11	1	-6	3784	3871
11	1	-5	2513	2595
11	1	-4	2116	2100
11	1	-3	5946	5772
11	1	-2	5321	5008
11	1	-1	3136	3001
11	1	0	4988	4624
11	1	1	3438	3447
11	1	2	4544	4574
11	1	3	2373	2012
11	1	4	720	659
11	1	5	2132	1904
11	1	6	2615	2957
11	1	7	727	729
12	0	-8	1228	1157
12	0	-6	4536	4529
12	0	-4	2895	2690
12	0	-2	6557	6212
12	0	0	7326	7918
12	0	2	5175	5007
12	0	4	2680	2633
12	0	6	2474	2567
12	2	-7	2492	2611
12	2	-6	1397	1069
12	2	-5	3776	3757
12	2	-4	3418	3479
12	2	-3	1465	1458
12	2	-2	614	320
12	2	-1	5672	5401
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12	2	1	3899	3708
12	2	2	1092	1167
12	2	3	1997	1972
12	2	4	1751	1870
12	2	5	2832	2823
12	4	-6	2446	1369
12	4	-5	2971	3102
12	4	-4	2905	2950
12	4	-3	1540	1536
12	4	-2	1447	1320
12	4	-1	4222	4047
12	4	0	2680	2613
12	4	1	2624	2801
12	4	2	965	924
12	4	3	3550	3532
12	4	4	2411	2429
12	6	-3	440	385
12	6	-2	2948	2910
12	6	-1	1459	1436
12	6	0	2977	3040
12	6	1	1018	904
13	5	-3	680	704
13	5	-2	2288	2270
13	5	-1	1033	977
13	5	0	2548	2706
13	5	1	930	967
13	3	-6	605	833
13	3	-5	3590	3792
13	3	-4	661	630
13	3	-3	3764	3718
13	3	-1	3893	3834
13	3	0	394	300
13	3	1	3272	3198
13	3	2	857	823
13	3	3	1192	1008
13	3	4	246	144
13	1	-7	1438	1466
13	1	-6	3090	3232
13	1	-5	1374	1419
13	1	-4	3185	3068
13	1	-3	3081	2792
13	1	-2	2751	2635
13	1	-1	3264	3036
13	1	0	4208	3950
13	1	1	3226	3894
13	1	2	2573	2553
13	1	3	880	826
13	1	4	2627	2718
13	1	5	1947	2033
14	0	-6	3675	3840
14	0	-4	1024	1035
14	0	-2	4363	4290
14	0	0	2734	2467
14	0	2	4304	4110
14	2	-5	2068	2091
14	2	-4	2503	2687
14	2	-3	3640	3736
14	2	-2	2382	2352
14	2	-1	4125	4041
14	2	0	2423	2342
14	2	1	2376	2246
14	2	2	508	266
14	2	3	1747	1705
14	4	-3	1424	1331
14	4	-2	2606	2609
14	4	-1	2049	2095
14	4	0	2458	2457
15	1	-4	2627	2600
15	1	-3	651	500
15	1	-2	3146	3125
15	1	-1	1250	1169
15	1	0	2062	2870
15	1	1	1284	1210

shown in Fig. 1, where the atomic numbering is also indicated, and are given with standard deviations in Table 3. The values have not been corrected for thermal motion.

Table 3. *Bond lengths and angles with their estimated standard deviations*

Se(1)–C(1)	1·930 (7) Å
Se(1)–O(1)	1·968 (7)
C(1) –C(2)	1·378 (10)
C(1) –C(6)	1·385 (10)
C(2) –C(3)	1·389 (13)
C(3) –C(4)	1·386 (14)
C(4) –C(5)	1·378 (14)
C(5) –C(6)	1·367 (13)
C(2) –C(7)	1·488 (11)
C(7) –O(1)	1·329 (12)
C(7) –O(2)	1·198 (10)
C(3) –H(3)	0·876 (109)
C(4) –H(4)	0·852 (92)
C(5) –H(5)	0·931 (108)
C(6) –H(6)	0·874 (84)
C(1) –Se(1)–O(1)	83·8 (3)°
C(1) –Se(1)–O(1′)	91·4 (3)
C(1) –Se(1)–C(1′)	101·0 (3)
O(1) –Se(1)–O(1′)	172·4 (3)
Se(1)–C(1) –C(2)	112·2 (5)
Se(1)–C(1) –C(6)	125·6 (6)
C(2) –C(1) –C(6)	122·2 (7)
C(1) –C(2) –C(3)	119·7 (7)
C(1) –C(2) - C(7)	116·4 (7)
C(3) –C(2) –C(7)	123·9 (7)
C(2) –C(3) –C(4)	118·3 (8)
C(3) –C(4) –C(5)	120·7 (10)
C(4) –C(5) –C(6)	121·6 (9)
C(1) –C(6) –C(5)	117·5 (7)
Se(1)–O(1) –C(7)	115·4 (5)
C(2) –C(7) –O(1)	112·1 (7)
C(2) –C(7) –O(2)	125·4 (8)
O(1) –C(7) –O(2)	122·4 (8)
C(2) –C(3) –H(3)	122·5 (77)
C(4) –C(3) –H(3)	119·0 (76)
C(3) –C(4) –H(4)	125·6 (55)
C(5) –C(4) –H(4)	113·5 (55)
C(4) –C(5) –H(5)	122·8 (67)
C(6) –C(5) –H(5)	114·5 (69)
C(1) –C(6) –H(6)	122·0 (56)
C(5) –C(6) –H(6)	120·5 (56)

The two symmetrical halves of the molecule are related by a twofold axis with the selenium atom in a special position. The configuration around the selenium atom is a trigonal bipyramid which is shown in the stereoscopic drawing in Fig. 2. The configuration is very similar to that found in the sulphur analogue, which has recently been studied by Kálmán, Sasvári & Kapovits (1973). The oxygen atoms, which are the most electronegative ligands, assume apical positions; the O–Se–O angle is 172·4°. Such an arrangement was predicted by Muetterties, Mahler, Packer & Schmutzler (1964) and has been observed in a number of compounds, as shown in Table 4. The Se–C distance of 1·930 Å compares well with earlier reported values (Aleby, 1972). The Se–O bond is 1·968 Å which is considerably longer than the 'normal' Se–O single bond length of 1·774 Å found in OCSeO. In the latter compound a ring closure has taken place by migration of the hydrogen atom from the carboxyl group to the selenoxide oxygen. The Se–O bond thus formed, which corresponds to the bond in SSP, is 2·378 Å.

The shorter Se–O bond in SSP has led to a substantial decrease of the valence angles at C(1), C(2) and C(7) in the five-membered ring as compared to OCSeO. The same phenomenon has been observed in the sulphur analogue although the standard deviations in that case are too large to allow a detailed comparison. The shorter Se–O distance has also led to a larger O–Se–O angle of 172·4°, compared with 169·9° in OCSeO. The Se–O bond in SSP cannot extend, because of short interactions with atoms in the identical half of the molecule. The distances from O(1) to H(6′) and C(6′) are 2·46 and 2·914 Å respectively, which may indicate a C–H· · ·O hydrogen bond.

The symmetrical halves of the molecule are nearly planar. The equation of the least-squares plane through the benzene ring is given in Table 5, together with the deviations from the plane. O(2) has the greatest deviation, 0·074 Å, from the plane of the benzene ring. The dihedral angle between these two benzene-ring planes of the molecule is 102·7°. The corresponding angle in the sulphur analogue is 106·7°. The molecules are held together by van der Waals forces only, with normal contact distances.

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Table 4. *Comparison with other compounds*

Compound	Type of interaction X-Y-Z	Angle X-Y-Z	Bond X-Y	Bond Y-Z	Reference
3,3′-Spirobi-(3-selenaphthalide)	O–Se–O	172·4°	1·968 Å	1·968 Å	This work
o-Carboxyphenyl methyl selenium oxide	O–Se–O	169·9	1·774	2·378	Dahlén (1973)
o-Nitrobenzeneselenyl thiocyanate	S–Se· · ·O	172·4	2·189	2·505	Eriksen & Hauge (1972)
o-Nitrobenzenesulfenic acid	O–S· · ·O	∼177	1·65	2·44	Hamilton & La Placa (1964)
o-Carboxyphenyl methyl sulphoxide	O–S· · ·O	175·6	1·517	2·777	Dahlén (1973)
(–) *o*-Carboxyphenyl methyl sulphoxide	O–S· · ·O	173·1	1·517	2·730	Dahlén (1974)
endo-3-Benzylsulphinylbicyclo[2,2,1]heptan-*endo*-2-carboxylic acid	O–S· · ·O	173·2	1·517	2·796	Zacharis (1974)

Table 5. *The least-squares plane through the carbon atoms in the benzene ring*

The equation is expressed in terms of the crystal axes:

$$-0{\cdot}6662X+0{\cdot}6378Y+0{\cdot}3866Z-0{\cdot}1559=0.$$

Deviations from the plane

C(1)	0·012 Å	C(6)	−0·009 Å
C(2)	−0·009	C(7)	−0·026
C(3)	−0·004	Se(1)	−0·018
C(4)	0·015	O(1)	−0·003
C(5)	−0·004	O(2)	−0·074

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The Crystal Structure and Phase Transition of Ammonium Hydrogen Bis-chloroacetate. II.* The Crystal Structure of the Ferroelectric Phase

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The crystal structure of the ferroelectric phase, below 128° K, of ammonium hydrogen bis-chloroacetate, $NH_4H(ClCH_2COO)_2$, has been determined by a three-dimensional X-ray analysis at 80 °K. The symmetry of the crystal changes from *C*2/*c* to *Cc*, and unit-cell parameters are $a=10{\cdot}47$, $b=11{\cdot}40$, $c=8{\cdot}22$ Å, $\beta=119{\cdot}3°$; $Z=4$. The structure was refined by the block-diagonal least-squares method using data collected on Weissenberg photographs. The final *R* is 0·106. The chloroacetate dimer retains almost the same conformation as that in the paraelectric phase including a very short hydrogen bond, 2·457 (16) Å. The nitrogen atom of the ammonium ion shifts by 0·240 Å from the twofold axis existing in the paraelectric phase. The mechanism of the ferroelectric phase transition is discussed.

Introduction

Ammonium hydrogen bis-chloroacetate (abbreviated to AHCA), $NH_4H(ClCH_2COO)_2$, exhibits ferroelectricity below 128 °K (Ichikawa & Mitsui, 1966). The crystal structure of the paraelectric phase was determined at room temperature (Ichikawa, 1972). In the paraelectric phase the two acidic radicals are crystallographically equivalent and are linked by a very short OHO hydrogen bond across the centre of symmetry. The present paper deals with a three-dimensional X-ray crystal structure analysis of the ferroelectric phase, carried out at 80 °K by the photographic method.

Experimental

All data were collected at 80 °K. A Weissenberg camera was put in a box, which was filled with dry nitrogen gas to prevent icing of the sample, and the temperature was controlled by blowing cold nitrogen gas over the sample (Itoh, Shiozaki, Hashiguchi & Mitsui, 1968). The temperature was measured by an Au:2·1 % Co–Cu thermocouple placed at about 1 mm from the crystal, and was maintained manually within ±2°. Weissenberg photographs were taken with Cu *Kα* radiation to determine the space group and unit-cell parameters. The systematic absences of reflexions are the same as those observed at room temperature and, because the crystal is now polar the space group changes from *C*2/*c* to *Cc*. Unit-cell parameters were determined from

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