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The Crystal Structure and Absolute Configuration of (−)-*o*-Carboxyphenyl Methyl Sulphoxide

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(−)-*o*-Carboxyphenyl methyl sulphoxide crystallizes in $P2_12_12_1$ with the cell dimensions $a=4{\cdot}841$, $b=11{\cdot}025$ and $c=15{\cdot}809$ Å. The absolute configuration was determined from the anomalous scattering of the sulphur and oxygen atoms. The final R value for the *S*- and *R*-configuration is 0·039 and 0·048 respectively for 725 observed reflexions. The molecular geometry is very close to that found in the racemic form of *o*-carboxyphenyl methyl sulphoxide but the quite different packing conditions have caused some differences. In the optically active form, for example, the molecule is almost planar, the carboxyl group is twisted only 2·6° out of the benzene ring while in the racemate the twist of the carboxyl group is 17·6°.

Introduction

The crystal structures of the racemic forms of *o*-carboxyphenyl methyl sulphoxide and its selenium analogue have recently been determined (Dahlén, 1973). Professor A. Fredga of Uppsala University who synthesized these racemates also resolved the sulphur compound into its optical antipodes, which is not possible for the selenium analogue. A single-crystal determination of the optically active (−)-*o*-carboxyphenyl methyl sulphoxide has been undertaken.

Experimental

Crystal data

Molecular formula	$C_8H_8O_3S$, (−)-*o*-carboxyphenyl methyl sulphoxide
Orthorhombic	$a=4{\cdot}841$ (1), $b=11{\cdot}025$ (3), $c=15{\cdot}809$ (3) Å
V	843·8 Å^3
M.W.	184·21
Z	4
D_c	1·450 g cm^{-3}
D_m	1·454 g cm^{-3}
Space group	$P2_12_12_1$ (systematic absences $h00$ with $h=2n+1$, $0k0$ with $k=2n+1$, $00l$ with $l=2n+1$)
Crystal dimensions	0·06 × 0·07 × 0·15 mm
λ	1·54051 Å (Cu $K\alpha$ radiation)
μ	30·34 cm^{-1} for Cu $K\alpha$ radiation.

The crystal used for the data collection was mounted along the a axis, which corresponded to the longest dimension of the crystal. Intensity data were recorded on a Picker FACS I automatic diffractometer using the Vanderbilt disc-oriented system by Dr P. G. Lenhert. Reflexions up to $2\theta=124°$ were measured in the θ–2θ scan mode with graphite monochromated Cu $K\alpha$ radiation. The intensities were scanned in 10 steps of 2 s with a scan width of 0·16°. Stationary background counts were taken on both sides of the peak. A set of 814 reflexions were obtained and 89 of these with $I<2\sigma(I)$ were considered as unobserved and excluded from the calculations. Data were corrected for the Lorentz and polarization factors, for secondary extinction but not for absorption.

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

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

(*a*) Heavy atoms

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
S(1)	2665 (2)	1570 (1)	2163 (1)	341 (5)	246 (5)	354 (5)	−12 (5)	−55 (6)	−35 (5)
C(1)	2030 (10)	−414 (4)	1042 (3)	346 (28)	308 (22)	342 (23)	−6 (19)	−47 (23)	19 (22)
C(2)	1214 (10)	766 (4)	1277 (3)	331 (24)	299 (23)	307 (25)	45 (20)	−34 (21)	−62 (23)
C(3)	−683 (11)	1382 (4)	788 (3)	449 (29)	335 (27)	417 (28)	23 (23)	−87 (25)	8 (26)
C(4)	−1760 (14)	869 (5)	63 (4)	693 (42)	550 (34)	530 (34)	41 (29)	−379 (34)	40 (31)
C(5)	−979 (14)	−285 (5)	−170 (4)	718 (41)	600 (35)	408 (30)	−105 (29)	−193 (32)	−47 (35)
C(6)	890 (13)	−919 (5)	306 (3)	618 (36)	395 (28)	376 (27)	−115 (24)	−113 (27)	38 (30)
C(7)	4021 (11)	−1174 (4)	1514 (3)	375 (26)	308 (25)	384 (27)	−30 (22)	9 (24)	−37 (23)
C(8)	526 (13)	969 (5)	2980 (4)	453 (33)	446 (31)	409 (33)	6 (25)	52 (27)	−61 (28)
O(1)	1643 (8)	2859 (3)	2044 (2)	565 (23)	214 (15)	558 (21)	−39 (15)	−199 (21)	19 (15)
O(2)	4956 (8)	−692 (3)	2221 (2)	563 (20)	289 (16)	508 (21)	−77 (16)	−212 (23)	104 (17)
O(3)	4725 (9)	−2176 (3)	1278 (2)	692 (28)	371 (20	516 (22)	−148 (17)	−118 (23)	141 (21)

Table 1 (*cont.*)

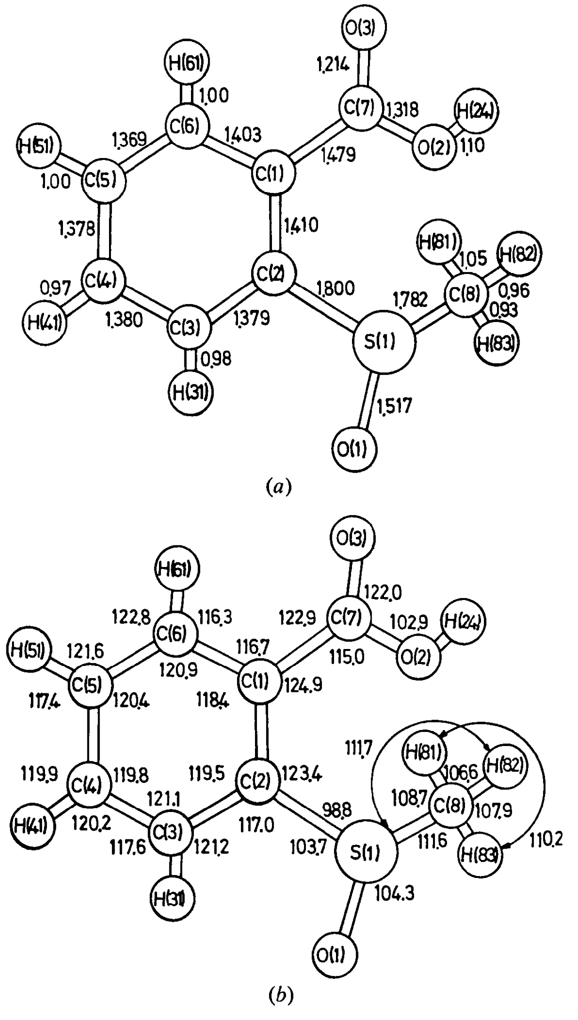
(*b*) Hydrogen atoms

	x	*y*	*z*	B (Å^2)
H(31)	−1399 (101)	2174 (39)	961 (26)	2·0 (0·9)
H(41)	−2991 (113)	1334 (44)	−298 (35)	4·1 (1·2)
H(51)	−2031 (156)	− 679 (55)	−642 (42)	6·5 (1·7)
H(61)	1599 (120)	−1737 (45)	138 (36)	4·9 (1·3)
H(81)	777 (141)	19 (57)	2997 (34)	5·6 (1·5)
H(82)	1059 (177)	1266 (59)	3461 (46)	7·4 (2·0)
H(83)	−1315 (149)	1164 (51)	2897 (40)	5·1 (1·5)
H(24)*	6413 (143)	1383 (55)	2452 (42)	6·9 (1·7)

* Refers to the oxygen atom O(2).

Structure determination and refinement

The position of the sulphur was obtained from a sharpened Patterson synthesis and after two rounds of structure-factor calculations and Fourier syntheses all non-hydrogen atoms were located. The R index at this stage was 0·24. Positional parameters and isotropic temperature factors were then refined with block-diagonal and full-matrix least-squares methods. At an R index of 0·09 a Fourier difference synthesis was calculated from which all hydrogen atoms could be located. The whole structure was then refined with full-matrix methods varying all positional parameters and anisotropic temperature factors for the non-hydrogen atoms and isotropic factors for the hydrogen atoms. Discrepancies between F_{obs} and F_{calc} for the strongest reflexions indicated secondary extinction effects. Corrections according to the formula given by Delaplane & Ibers (1969) were therefore performed.



(*a*)

(*b*)

Fig. 1. (*a*) Bond lengths and (*b*) angles.

As it was of interest to establish the absolute configuration, the sulphur and oxygen atoms were corrected for anomalous dispersion with the values given by Cromer & Liberman (1970). The enantiomer chosen from the Fourier synthesis was then refined to a final R value of 0·039. The average ratio between shifts and standard deviations at the end of the refinement was 0·01 for the non-hydrogen atoms and 0·04 for the hydrogen atoms. The weighting scheme used in the least-squares refinement was (Mills & Rollett, 1961)

$$w = 1 + [(|F_o| - 5\cdot 3|F_{\text{min}}|)/3\cdot 7|F_{\text{min}}|]^2 \ .$$

Atomic scattering factors used for carbon, oxygen and sulphur atoms were those in *International Tables for X-ray Crystallography* (1962) and for hydrogen atoms those of Stewart, Davidson & Simpson (1965). All calculations were performed on a Datasaab D21-PDP15 dual computer with a program system developed at this institute.

Results and discussion

As the sulphur environment is asymmetric it was of interest to establish the absolute configuration. All indices were therefore changed from hkl to $h\bar{k}l$ and a structure-factor calculation based on the latter data set gave an R index of 0·048. The enantiomer chosen from the sulphur-phased Fourier synthesis which was shown to have the S configuration thus gave a final R index of 0·039 while the corresponding R value for the R enantiomer was 0·048. An application of Hamilton's (1965) generalized R index test showed that the S configuration agrees better with the experimental data at the 99·999% level of significance. The conclusion that (−)-*o*-carboxyphenyl methyl sulphoxide has the S configuration has also been made by Barbieri, Davoli, Moretti, Montanari & Torre (1969) during studies of asymmetric induction in oxidation of optically active esters of *o*-(methylthio)benzoic acid.

The final atomic parameters are given in Table 1. Table 2 gives the observed and calculated structure factors. Interatomic distances and angles are shown in Fig. 1 and with standard deviations in Table 3. The values have not been corrected for thermal motion. The intermolecular distances and angles are very close to those found in the racemic analogue.

In both the optically active form and the racemate there is a short intramolecular contact between S(1) and O(2) which has led to a considerable opening of the angles at C(2), C(1) and C(7). The quite different packing conditions have caused some differences, however, in the molecular geometry of the two molecules. In the racemate the carboxyl group is twisted 17·1° out of the plane of the benzene ring resulting in a S···O contact of 2·777 Å. The optically active molecule on the other hand is more planar. The equation of the least-squares planes through the benzene ring and the deviations from this plane for all heavier atoms are given in

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

H	K	L	FOBS	FCALC
0	0	2	5595	5555
0	0	4	4305	4509
0	0	6	382	317
0	0	8	2251	2232
0	0	10	3984	3804
0	0	12	3675	3714
0	0	14	2953	2994
0	0	16	1657	1718
0	0	18	426	478
0	1	17	357	303
0	1	15	651	579
0	1	14	764	738
0	1	13	693	908
0	1	12	1440	1402
0	1	10	2058	2807
0	1	9	2289	2102
0	1	8	2540	2527
0	1	7	5030	5500
0	1	6	535	401
0	1	5	4054	3992
0	1	3	500	522
0	1	2	8132	7059
0	1	1	435	422
0	2	0	1420	1438
0	2	1	2615	2804
0	2	2	4962	5149
0	2	3	1983	2079
0	2	4	1545	1509
0	2	5	1917	1936
0	2	6	611	805
0	2	7	460	402
0	2	8	1471	1304
0	2	9	2653	2593
0	2	11	1216	1249
0	2	12	1227	1215
0	2	13	1730	1733
0	2	14	1359	1025
0	2	15	1330	1304
0	2	16	271	67
0	3	17	934	1031
0	3	16	616	826
0	3	15	970	1074
0	3	14	1081	934
0	3	12	1485	1517
0	3	10	2570	2052
0	3	9	311	177
0	3	8	967	933
0	3	7	3983	3677
0	3	6	2109	2133
0	3	5	4034	4742
0	3	4	379	529
0	3	3	2115	2094
0	3	2	3256	3301
0	3	1	800	801
0	4	0	5235	5403
0	4	1	1720	1834
0	4	2	1931	2042
0	4	3	2678	2743
0	4	4	2618	2625
0	4	5	3692	3508
0	4	6	483	449
0	4	7	993	1000
0	4	8	923	924
0	4	9	1063	1043
0	4	14	1654	1634
0	4	15	1408	1415
0	4	16	1201	1179
0	4	17	1864	1877
0	5	15	451	433
0	5	14	925	819
0	5	13	882	900
0	5	11	1380	1327
0	5	10	420	530
0	5	9	3358	3329
0	5	8	1472	1394
0	5	7	4306	4005
0	5	6	1898	1831
0	5	5	2054	2050
0	5	3	1551	1587
0	5	2	1027	808
0	5	1	3073	3020
0	6	0	1604	1544
0	6	1	4739	4670
0	6	2	1550	1550
0	6	3	1204	1190
0	6	4	1126	1131
0	6	5	783	775
0	6	6	1594	1609
0	6	7	1542	1529
0	6	8	1300	1389
0	6	9	2067	2135
0	6	10	797	771
0	6	11	1647	1601
0	6	13	1222	1240
0	6	14	645	796
0	7	14	301	253
0	7	12	692	807
0	7	11	1738	1601
0	7	10	882	915
0	7	8	2357	2425
0	7	7	1597	1519
0	7	6	3314	3327
0	7	5	2040	2049
0	7	4	2221	2202
0	7	3	2327	2350
0	7	1	381	302
0	8	0	1155	1034
0	8	1	3994	3948
0	8	2	620	758
0	8	3	2079	2001
0	8	4	679	695
0	8	5	1758	1603
0	8	6	380	407
0	8	7	380	507
0	8	8	775	796
0	8	10	1004	974
0	8	11	1339	1204
0	8	12	858	799
0	8	13	1378	1434
0	9	11	798	969
0	9	10	1305	1358
0	9	9	473	524
0	9	8	3427	3309
0	9	7	2405	2439
0	9	6	3211	3155
0	9	5	1015	972
0	9	4	2390	2424
0	9	3	586	538
0	9	2	939	891
0	10	0	969	999
0	10	1	1753	1810
0	10	2	1396	1357
0	10	3	374	111
0	10	4	706	740
0	10	5	1281	1267
0	10	6	1525	1479
0	10	8	343	101
0	10	10	704	724
0	10	11	671	603
0	11	8	763	804
0	11	7	363	211
0	11	6	473	519
0	11	5	401	448
0	11	3	1116	1001
0	11	2	755	708
0	11	1	1257	1103
0	12	0	544	501
0	12	1	356	478
0	12	2	672	407
0	12	3	253	112
0	12	4	1440	1363
1	12	4	517	455
1	12	3	748	809
1	12	2	441	393
1	12	0	556	538
1	11	1	1777	1603
1	11	2	341	209
1	11	3	761	772
1	11	5	599	401
1	11	7	419	801
1	11	8	507	592
1	10	10	1236	1194
1	10	9	694	693
1	10	8	1090	1017
1	10	7	1135	1101
1	10	6	1096	1064
1	10	5	574	605
1	10	4	1481	1477
1	10	3	1974	2044
1	10	2	908	921
1	10	1	677	794
1	9	0	2575	2539
1	9	1	539	823
1	9	2	1911	1979
1	9	3	1705	1719
1	9	4	1541	1506
1	9	5	1112	1095
1	9	6	964	1034
1	9	7	977	691
1	9	8	792	853
1	9	10	1475	1571
1	9	12	1227	1212
1	8	13	541	574
1	8	12	465	539
1	8	11	1175	1107
1	8	9	2094	2107
1	8	8	1340	1397
1	8	7	2084	2000
1	8	6	573	503
1	8	5	4141	4119
1	8	4	750	674
1	8	3	1395	1309
1	8	2	782	767
1	8	1	1142	1231
1	8	0	1919	1702
1	7	0	2369	2305
1	7	1	1573	1641
1	7	2	2943	2891
1	7	3	2696	2044
1	7	4	2459	2305
1	7	5	592	708
1	7	6	1381	1302
1	7	7	1648	1437
1	7	8	776	843
1	7	9	658	601
1	7	10	1246	1323
1	7	11	481	339
1	7	12	1040	1132
1	7	13	1021	902
1	7	14	1297	1332
1	6	14	472	571
1	6	12	1027	1001
1	6	11	1198	1102
1	6	10	1386	1306
1	6	9	1519	1533
1	6	8	2424	2433
1	6	7	2224	2173
1	6	6	2900	2898
1	6	5	682	829
1	6	4	2061	2044
1	6	3	1944	1905
1	6	2	461	425
1	6	1	372	231
1	6	0	900	834
1	5	0	1229	1200
1	5	1	3331	3390
1	5	2	1324	1227
1	5	3	1693	1814
1	5	4	1957	1919
1	5	5	2311	2299
1	5	6	1083	1044
1	5	7	1149	1102
1	5	8	819	761
1	5	9	348	427
1	5	10	1901	1805
1	5	11	1711	1709
1	5	12	500	605
1	5	13	919	1023
1	5	14	556	420
1	5	15	1279	1307
1	4	15	499	658
1	4	14	1515	1509
1	4	13	532	832
1	4	12	1577	1507
1	4	11	994	905
1	4	10	1533	1537
1	4	9	1094	1395
1	4	8	953	1013
1	4	7	1594	1594
1	4	6	1336	1309
1	4	5	1093	1710
1	4	4	2712	2609
1	4	3	2653	2527
1	4	2	4389	4207
1	4	1	913	921
1	4	0	1091	1722
1	3	0	2047	2891
1	3	1	1759	1738
1	3	2	2776	2898
1	3	3	1370	2139
1	3	4	3151	3199
1	3	5	1491	1421
1	3	6	684	509
1	3	7	1791	1737
1	3	9	972	894
1	3	10	477	392
1	3	11	673	579
1	3	12	1739	1774
1	3	13	1171	1193
1	3	14	1980	1902
1	3	15	483	419
1	3	16	1289	1234
1	2	16	644	652
1	2	15	815	821
1	2	14	1194	1299
1	2	13	682	839
1	2	12	634	801
1	2	11	2176	2182
1	2	10	516	527
1	2	9	2105	2199
1	2	8	1585	1692
1	2	7	3192	3124
1	2	6	3441	3371
1	2	5	3383	3302
1	2	4	4770	4773
1	2	3	3980	4003
1	2	2	5170	3192
1	2	1	2792	2791
1	2	0	6013	6793
1	1	0	4263	4308
1	1	1	6408	6604
1	1	2	6372	6509
1	1	3	8050	8477
1	1	4	2419	2515
1	1	5	2376	2493
1	1	6	2580	2549
1	1	7	2624	2828
1	1	8	711	507
1	1	9	1947	1923
1	1	10	549	405
1	1	11	2373	2320
1	1	12	2140	2726
1	1	13	2282	2209
1	1	14	387	777
1	1	15	982	904
1	1	16	1097	1133
1	1	17	616	841
1	0	15	339	297
1	0	15	350	495
1	0	14	280	115
1	0	12	784	704
1	0	11	485	492
1	0	10	3811	3901
1	0	9	2413	2435
1	0	8	3013	2907
1	0	7	1261	1221
1	0	6	3511	3554
1	0	5	1584	1502
1	0	4	4075	4347
1	0	3	1929	1938
1	0	2	7141	7177
1	0	1	456	409
2	0	1	1312	1378
2	0	2	1459	1557
2	0	3	440	364
2	0	4	2323	2397
2	0	5	956	891
2	0	6	451	402
2	0	7	663	645
2	0	8	580	555
2	0	9	340	158
2	0	10	1957	1935
2	0	11	648	672
2	0	12	629	613
2	0	13	1748	1690
2	0	14	800	751
2	0	16	934	951
2	1	16	408	369
2	1	15	661	500
2	1	12	960	944
2	1	11	2587	2508
2	1	10	920	907
2	1	9	3009	2974
2	1	8	1129	1145
2	1	7	2034	2013
2	1	6	1333	1338
2	1	5	4107	3935
2	1	4	1499	1548
2	1	3	4181	4094
2	1	2	2644	2518
2	1	1	2394	2404
2	1	0	1295	1247
2	2	0	1536	1509
2	2	1	3504	3677
2	2	2	3257	3251
2	2	3	3384	3342
2	2	4	3913	3821
2	2	5	3251	3198
2	2	6	3245	3158
2	2	7	680	853
2	2	8	2085	2018
2	2	9	870	878
2	2	10	584	508
2	2	11	1290	1341
2	2	12	1381	1315
2	2	13	1535	1541
2	2	14	619	808
2	2	15	1390	1307
2	2	16	950	935
2	3	16	352	391
2	3	15	880	844
2	3	14	520	341
2	3	13	742	818
2	3	12	1380	1301
2	3	11	1080	1108
2	3	10	1370	1391
2	3	9	686	879
2	3	8	2585	2551
2	3	7	1586	1217
2	3	6	3383	3371
2	3	5	3481	3429
2	3	4	3763	3361
2	3	3	686	897
2	3	2	1189	1003
2	3	1	2730	2709
2	3	0	1137	907
2	4	0	912	967
2	4	1	1524	1551
2	4	2	1412	1452
2	4	3	1059	1421
2	4	4	1020	1505
2	4	5	763	824
2	4	7	1787	1725
2	4	8	1287	1203
2	4	9	359	443
2	4	11	1174	1131
2	4	12	1197	1201
2	4	13	1207	1149
2	4	14	976	905
2	4	15	392	404
2	5	15	341	477
2	5	14	971	968
2	5	13	789	405
2	5	12	870	904
2	5	11	1470	1401
2	5	10	436	405
2	5	9	1479	1403
2	5	8	579	308
2	5	7	1040	1158
2	5	6	979	974
2	5	5	939	1102
2	5	4	651	835
2	5	3	1265	1299
2	5	2	621	408
2	5	1	1280	1291
2	5	0	1359	1352
2	6	0	5380	5351
2	6	1	729	825
2	6	2	3010	3503
2	6	3	687	763
2	6	4	2041	2145
2	6	6	570	451
2	6	7	570	522
2	6	9	596	412
2	6	10	989	748
2	6	11	792	792
2	6	12	1795	1403
2	6	13	550	551
2	6	14	1507	1292
2	7	15	333	405
2	7	12	950	905
2	7	11	697	725
2	7	10	2138	2804
2	7	9	753	751
2	7	8	1085	1808
2	7	7	1210	1239
2	7	6	1045	1807
2	7	5	1095	1105
2	7	4	2751	2751
2	7	3	921	905
2	7	2	2082	2142
2	7	1	576	501
2	7	0	652	644
2	8	0	422	222
2	8	1	1089	1909
2	8	2	992	931
2	8	3	3127	3001
2	8	4	627	657
2	8	5	931	942
2	8	6	989	1102
2	8	9	1289	1314
2	8	11	892	852
2	9	10	1121	1105
2	9	8	976	998
2	9	7	480	378
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2	9	5	939	910
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2	9	3	444	422
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2	9	0	873	732
2	10	0	1811	1824
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2	10	2	1392	1322
2	10	3	1076	949
2	10	4	545	552
2	10	5	1316	1259
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2	10	7	584	801
2	10	8	651	594
2	11	5	1357	1358
2	11	4	472	516
2	11	3	552	601
2	11	2	448	502
2	11	1	770	809
2	11	0	896	827
3	10	5	615	947
3	10	4	481	501
3	10	2	980	1021
3	10	1	480	428
3	10	0	393	507
3	9	0	2212	2177
3	9	1	1114	1178
3	9	2	1343	1308
3	9	3	442	334
3	9	4	632	514
3	9	8	345	302
3	8	10	384	234
3	8	9	976	874
3	8	8	380	305
3	8	7	1553	1575
3	8	5	553	821
3	8	4	346	40
3	8	3	981	954
3	8	2	587	503
3	8	1	1152	1105
3	7	0	2611	2601
3	7	1	1183	1222
3	7	2	1310	1274
3	7	3	1595	1551
3	7	4	570	802
3	7	5	687	771
3	7	6	615	627
3	7	8	442	479
3	7	9	1170	1139
3	7	10	683	623
3	7	11	1021	1044
3	6	12	872	801
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3	4	13	720	772
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3	4	9	1044	1807
3	4	8	1982	1906
3	4	7	1190	1067
3	4	6	1970	1953
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3	4	2	599	576
3	4	1	1976	1901
3	4	0	923	904
3	3	0	1529	1601
3	3	1	721	675
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3	3	4	1753	1756
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3	3	10	844	839
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3	3	12	760	801
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3	2	12	1001	930
3	2	11	1290	1105
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3	2	2	1675	1915
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3	1	0	553	561
3	1	1	3096	3003
3	1	2	536	634
3	1	3	755	789
3	1	4	1018	1095
3	1	5	1027	908
3	1	6	1354	1313
3	1	7	509	541
3	1	8	697	514
3	1	9	1374	1336
3	1	10	1486	1306
3	1	11	541	390
3	1	12	353	320
3	1	13	786	856
3	1	14	537	590
3	1	15	1146	1152
3	0	15	410	397
3	0	12	524	548
3	0	11	840	934
3	0	9	626	829
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3	0	7	1130	1054
3	0	6	2625	2607
3	0	5	461	445
3	0	4	1797	1794
3	0	3	634	672
3	0	2	529	534
3	0	1	2031	1934
4	0	0	1173	1201
4	0	1	930	701
4	0	2	2316	2306
4	0	3	980	1002
4	0	4	1339	1303
4	0	5	914	945
4	0	6	1430	1418
4	0	8	621	552
4	0	9	414	252
4	0	10	757	725
4	0	12	1018	1034
4	1	12	459	445
4	1	11	1051	1049
4	1	10	657	709
4	1	9	412	326
4	1	8	1426	1405
4	1	7	1476	1307
4	1	6	1708	1624
4	1	5	1449	1434
4	1	4	767	765
4	1	3	1082	1074
4	1	2	743	651
4	1	1	492	302
4	1	0	390	872
4	2	0	897	838
4	2	1	1355	1278
4	2	2	497	413
4	2	3	1490	1438
4	2	4	987	918
4	2	5	917	809
4	2	7	777	721
4	2	8	659	663
4	2	9	413	372
4	2	10	774	701
4	2	11	450	404
4	2	12	511	413
4	3	11	744	695
4	3	10	1267	1299
4	3	9	678	663
4	3	8	1537	1406
4	3	6	1352	1317
4	3	5	449	451
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4	3	0	1070	1135
4	4	0	643	670
4	4	1	1922	1930
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4	4	4	1745	1826
4	4	5	746	915
4	4	6	1276	1207
4	4	7	524	503
4	4	8	569	493
4	4	9	839	801
4	4	10	682	701
4	4	11	745	789
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4	5	7	1373	1391
4	5	6	351	396
4	5	5	1110	1108
4	5	4	774	802
4	5	3	1727	1690
4	5	2	1518	1541
4	5	1	779	706
4	6	0	1576	1614
4	6	1	1070	1062
4	6	2	1113	1123
4	6	3	1191	1111
4	6	4	561	504
4	6	5	550	599
4	6	7	735	753
4	6	8	587	543
4	6	9	347	510
4	7	7	891	854
4	7	6	618	604
4	7	5	782	802
4	7	4	429	307
4	7	3	429	490
4	7	2	338	430
4	8	0	350	424
4	8	1	1243	1250
4	8	2	345	357
4	8	3	788	900
4	8	4	457	300
4	8	5	381	255
5	5	1	1087	1172
5	5	2	404	301
5	5	3	848	895
5	4	5	932	949
5	4	4	1214	1318
5	4	3	796	787
5	4	1	491	592
5	4	0	348	417
5	3	0	1276	1354
5	3	1	513	510
5	3	2	1547	1509
5	3	3	698	785
5	3	4	920	815
5	3	6	619	700
5	2	7	695	679
5	2	5	1102	1100
5	2	4	455	655
5	2	3	516	480
5	2	2	879	791
5	2	0	886	904
5	1	0	781	851
5	1	1	661	629
5	1	2	1010	937
5	1	3	1042	1078
5	1	4	890	932
5	1	5	666	798
5	1	7	531	503
5	0	6	585	628
5	0	5	494	517
5	0	4	590	527
5	0	3	643	674
5	0	1	819	792

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

S(1) -C(2)	1·800 (5) Å	C(2)—S(1) -C(8)	98·8 (2)°
S(1) -C(8)	1·782 (6)	C(2)—S(1) -O(1)	103·7 (2)
S(1) -O(1)	1·517 (3)	C(8)—S(1) -O(1)	104·4 (2)
C(1)–C(2)	1·410 (6)	S(1) —C(2)–C(1)	123·4 (4)
C(2)–C(3)	1·379 (7)	S(1) —C(2)–C(3)	117·0 (3)
C(3)–C(4)	1·380 (8)	C(1)—C(2)–C(3)	119·5 (4)
C(4)–C(5)	1·378 (8)	C(2)—C(3)–C(4)	121·1 (5)
C(5)–C(6)	1·369 (9)	C(3)—C(4)–C(5)	119·8 (5)
C(1)–C(6)	1·403 (7)	C(4)—C(5)–C(6)	120·4 (5)
C(1)–C(7)	1·479 (7)	C(1)—C(6)–C(5)	120·9 (5)
C(7)–O(2)	1·318 (6)	C(2)—C(1)–C(6)	118·4 (4)
C(7)–O(3)	1·214 (6)	C(2)—C(1)–C(7)	124·9 (4)
C(3)–H(31)	0·978 (44)	C(6)—C(1)–C(7)	116·7 (4)
C(4)–H(41)	0·972 (54)	C(1)—C(7)–O(2)	115·0 (4)
C(5)–H(51)	1·003 (68)	C(1)—C(7)–O(3)	122·9 (5)
C(6)–H(61)	1·000 (52)	O(2)—C(7)–O(3)	122·0 (5)
C(8)–H(81)	1·055 (63)	C(2)—C(3)–H(31)	121·2 (26)
C(8)–H(82)	0·957 (73)	C(4)—C(3)–H(31)	117·6 (26)
H(8)–H(83)	0·926 (72)	C(3)—C(4)–H(41)	120·2 (31)
O(2)–H(24)	1·101 (65)	C(5)—C(4)–H(41)	119·9 (31)
		C(4)—C(5)–H(51)	117·4 (38)
		C(6)—C(5)–H(51)	121·6 (37)
		C(1)—C(6)–H(61)	116·3 (33)
		C(5)—C(6)–H(61)	122·8 (33)
		S(1) —C(8)–H(81)	108·7 (33)
		S(1) —C(8)–H(82)	111·6 (47)
		S(1) —C(8)–H(83)	111·7 (39)
		H(81)–C(8)–H(82)	106·6 (50)
		H(81)–C(8)–H(83)	110·2 (51)
		H(82)–C(8)–H(83)	107·9 (63)
		C(7)—O(2)–H(24)	102·9 (34)

Table 4. The twist of the carboxyl group is only 2·6° which has led to a S· · ·O distance of 2·730 Å. In this case the carboxyl group has no possibility of twisting more as the oxygen atom O(3) is enclosed between the methyl hydrogens H(82) and H(83) in the hydrogen-bonded molecule (see below) and the benzene ring hydrogens H(5) and H(6) in the molecule related by a twofold screw in the **a** direction. The packing arrangement is shown in Fig. 2, with the closer contacts indicated, and in the stereoscopic drawing in Fig. 3. As in the racemate the molecules are linked together by a hydrogen bond between O(1) and O(2) in the molecule related by a twofold screw axis along **b**. The O(1)· · ·O(2) and the O(1)· · ·H(24) distances are 2·572 and 1·49 Å respectively and the O(1)· · ·H(24)–O(2) angle is 166°.

Table 4. *Least-squares plane through the carbon atoms in the benzene ring*

The equation, expressed in terms of the crystal axes, is:

$$0{\cdot}3556X + 0{\cdot}4159Y - 0{\cdot}8370Z + 0{\cdot}0322 = 0.$$

Deviations from the plane

C(1)	−0·001 Å	C(7)	−0·003 Å
C(2)	0·003	O(2)	−0·063
C(3)	−0·006	O(3)	0·029
C(4)	0·005	S(1)	0·114
C(5)	−0·002	O(1)	0·392
C(6)	0·000	C(8)	−1·613

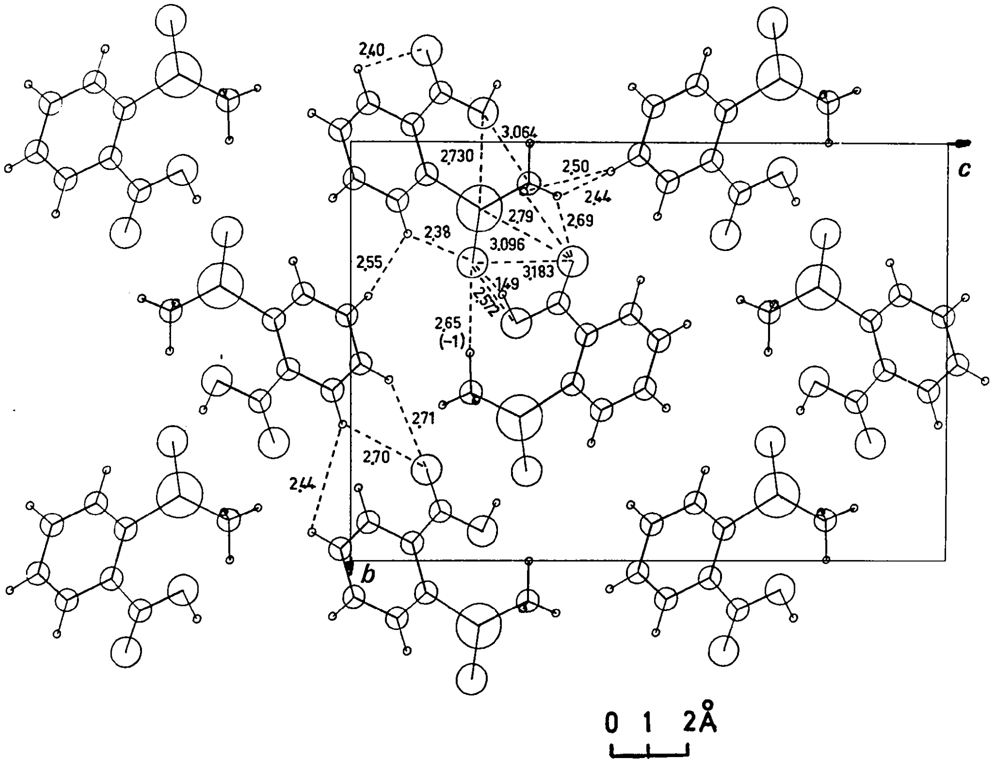

Fig. 2. The molecular packing seen along the *a* axis.

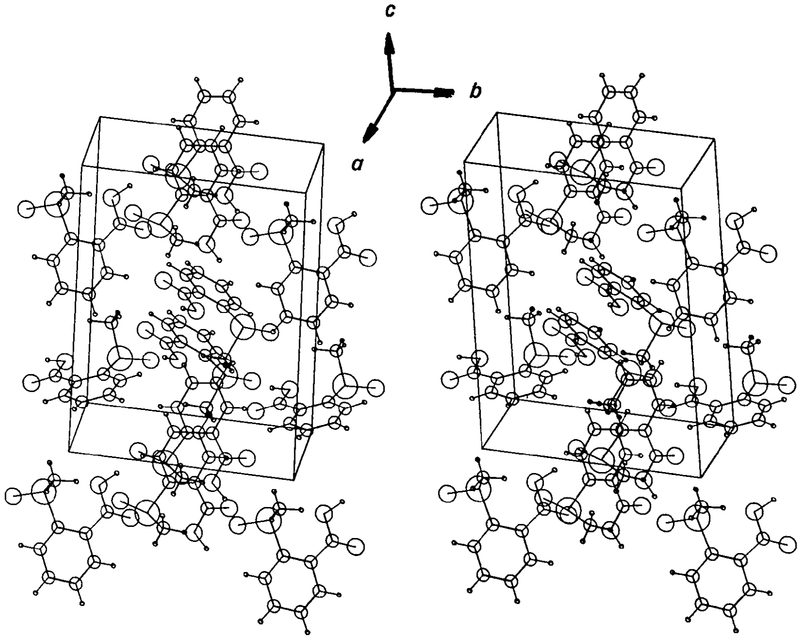

Fig. 3. Stereoscopic view of (−)-*o*-carboxyphenyl methyl sulphoxide.

In the racemate (space group $P2_1/c$) the two enantiomers are packed with the methyl group in one molecule pointing towards the benzene ring in the other and *vice versa*. In the optically active form with only the *S* enantiomer present the packing arrangement is quite different owing to the presence of the additional screw axes in the **a** and **c** directions. The *a* axis is 4·841 Å which, with the tilt of the benzene rings of 48·5° to the (100) plane, gives a benzene-ring separation of 3·63 Å. Benzene rings may pack as close as 3·4 Å (Pauling, 1960) but this is not possible in this case as O(1), which is participating in the hydrogen bond, is in very close contact (2·65 Å) with H(81) in the hydrogen-bonded molecule translated one unit in **a**. Benzene rings are also in contact with perpendicular planes in the **b** direction with a shortest hydrogen–hydrogen distance of 2·55 Å. The packing arrangement in the optically active form is somewhat less effective than in the racemate. The volume per molecule is 211·0 Å^3 as compared with 208·2 Å^3 in the racemate.

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