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The Crystal Structure of Ammonium Acid *o*-Carboxybenzenesulfonate, $NH_4(C_6H_4COOH.SO_3)$

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Crystals of ammonium acid *o*-carboxybenzenesulfonate crystallize in the orthorhombic system with $a=7{\cdot}04_5\pm0{\cdot}003$, $b=10{\cdot}53_5\pm0{\cdot}003$, $c=25{\cdot}51_5\pm0{\cdot}005$ Å; the space group is *Pcab*. The structure was determined by using three-dimensional intensity data collected on a computer-controlled diffractometer operated in a closed-loop manner by a stored data collection program in an IBM 1620 computer. The structure is ionic, consisting of ammonium ions and infinite chains of acid *o*-carboxybenzenesulfonate ions; the chains are formed by short O–H···O bonds of $2{\cdot}64_0$ Å from carboxyl groups to sulfonate groups through the *a*-glide planes perpendicular to the *b* axis. The locations of hydrogen atoms substantiate the chemical formula $NH_4(C_6H_4 . COOH . SO_3)$ and the compound is named accordingly. The benzene ring is a slightly distorted hexagon with one relatively short C–C bond of $1{\cdot}37_0$ Å; the average of the remaining five C–C bond distances is 1·387 Å, and the average of the six angles is 120·0°. The carboxyl group makes an angle of 50·7° with the benzene ring. Other effects of steric hindrance include shifts of the sulfur atom and the carboxyl carbon from the benzene ring plane and also deviations of angles around the ring carbon atoms associated with the derivative groups from the normal value. Bond distances and angles in the carboxyl and sulfonate groups are normal.

Introduction

The crystal structure of ammonium acid *o*-sulfobenzoate, or more correctly acid *o*-carboxybenzenesulfonate, was investigated as a part of our study on *ortho*-substituted benzoic acids and their salts. The work is the third in the series, ammonium (Okaya & Pepinsky, 1957) and potassium acid phthalates (Okaya, 1965) having been reported. The main purpose of such studies is to obtain information about the effect of steric hindrance on the aromatic system by varying size and nature of derivative groups.

Ammonium acid *o*-carboxybenzenesulfonate belongs to a series of acid alkali salts of phthalic acid and *o*-sulfobenzoic acid or *o*-carboxybenzenesulfonic acid; these salts crystallize in the orthorhombic system and are listed by Groth (1917). From the axial ratios, crystal habit and cleavages given by the morphological studies, these crystals are expected to possess similar structures. For example, the main features of structure building made by the packing of aromatic rings and the hydrogen-bond formation are the same for ammonium (*Pcab*) and potassium ($P2_1ab$) acid phthalates; the difference in the space groups of these two salts is the result of differences in the manner in which the cations connect the aromatic ions.

Experimental

A single crystal of ammonium acid *o*-carboxybenzenesulfonate was ground into an approximately spherical shape and mounted on a General Electric Goniostat which was placed on a Picker biplane diffractometer; this belongs to CCXD, a computer-controlled diffractometer system (Cole, Okaya & Chambers, 1963) which is operated in a closed-loop manner by an IBM 1620 computer under a stored data collection program (Okaya, 1964, 1966). The unit-cell dimensions were determined on the diffractometer by using Mo $K\alpha$ radiation and used as input parameters for the data collection programs; they are $a=7{\cdot}04_5\pm0{\cdot}003$, $b=10{\cdot}53_5\pm0{\cdot}003$, and $c=25{\cdot}51_5\pm0{\cdot}005$ Å. The crystals belong to the orthorhombic class with space group *Pcab*; ammonium acid phthalate also crystallizes in this space group with $a=6{\cdot}40$, $b=10{\cdot}23$ and $c=26{\cdot}14$ Å (Okaya & Pepinsky, 1957). There are eight chemical units of the formula $NH_4(C_6H_4{\cdot}COOH{\cdot}SO_3)$ in a unit cell ($\varrho_{obs}=1{\cdot}523$, Groth). Three-dimensional integrated intensity data were obtained from the specimen by using filtered Mo $K\alpha$ radiation. For each reflection, the alignment of the crystal was first checked by optimizing the ω setting; the intensity data were then taken by step-scanning around the 2θ axis. The number of steps for the $(\theta-2\theta)$ scanning was 24 with intervals of 0·07° for $2\theta\leq40°$ and 0·09° for higher 2θ values. In the course of the ω scanning, the minimum and maximum counts were recorded for each reflection and if the difference between them was less than the statistical fluctuation, the reflection was treated as a non-observed one. All non-equivalent reflections (about 2800) within the range of $\sin\theta/\lambda\leq0{\cdot}85$ were studied in this fashion and 2583 reflections were recorded as observed ones. The general programming technique for such computer-controlled data collection tasks is explained elsewhere (Okaya, 1966); copies of the detailed computer programs used by the present study are also available from the author (1964). The integrated intensity was calculated from the $(\theta-2\theta)$ step-scanning

data on the IBM 1620 computer as a time-shared program. Owing to the small size of the specimen, no absorption correction was made to the intensity data.

Structure determination and refinement

The crystal structure of ammonium acid *o*-carboxybenzenesulfonate was determined and refined in the usual manner by using the three-dimensional intensity data thus obtained. The position of the sulfur atom was obtained from a sharpened three-dimensional Patterson function and the positions of other nonhydrogen atoms were derived from an approximate three-dimensional density function calculated with the phases assigned by the contribution of the sulfur atom. The structure was then refined by the least-squares methods first by using a block-diagonal approximation and then a full-matrix program on an IBM 7094 computer (Okaya, 1963). The positions of hydrogen atoms in the aromatic ion were determined in the course of the refinement by the usual (F_o-F_c) synthesis method and refined with isotropic temperature factors. The difference synthesis showed smearing of the density around the nitrogen atom of the ammonium ion and no effort was made to locate the hydrogen atoms of the ion. The final conventional error factor, $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$, was 0·060 for the observed reflections. The shifts of parameters in the final stage were almost

Table 1

(*a*) Atomic coordinates in fractions of cell edges and their standard deviations in 10^{-4} Å.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
NH_4^+	0·69062	27	0·12177	26	0·02801	28
S	0·16759	6	0·06241	6	0·08477	6
O(1)	0·28435	23	0·10823	20	0·04228	19
O(2)	0·01317	25	0·14690	30	0·09636	28
O(3)	0·10928	28	−0·06810	21	0·07580	23
C(I)	0·48170	28	−0·14283	27	0·11513	27
O(I)	0·46178	29	−0·25560	22	0·13705	22
O(I′)	0·53409	29	−0·12690	24	0·07091	22
C(1)	0·43878	29	−0·03741	26	0·15245	25
C(2)	0·54199	34	−0·03485	36	0·19846	30
C(3)	0·52247	38	0·06565	39	0·23348	31
C(4)	0·39889	33	0·16245	31	0·22242	29
C(5)	0·29310	31	0·16036	27	0·17635	28
C(6)	0·31252	25	0·06038	23	0·14168	24
H(O)	0·485		−0·319		0·109	
H(2)	0·635		−0·105		0·205	
H(3)	0·584		0·072		0·265	
H(4)	0·336		0·217		0·249	
H(5)	0·218		0·230		0·164	

(*b*) Anisotropic thermal parameters.
The β's are used in the expression: $\exp\{-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
NH_4^+	0·017328	0·007176	0·001336	−0·000211	−0·000947	−0·001877
S	0·012978	0·005083	0·000936	0·001438	−0·000568	−0·000062
O(1)	0·020060	0·006270	0·000966	−0·001338	−0·000574	0·001091
O(2)	0·017398	0·012148	0·001754	0·012789	−0·002268	−0·002586
O(3)	0·022459	0·006543	0·001356	−0·009946	−0·000823	−0·000118
C(I)	0·016125	0·005835	0·001111	0·005592	0·000270	0·000815
O(I)	0·029003	0·005881	0·001405	0·006583	0·003211	0·000867
O(I′)	0·029203	0·007911	0·001092	0·009503	0·002227	0·000932
C(1)	0·016265	0·005761	0·000887	0·001923	0·000039	0·000617
C(2)	0·019449	0·009147	0·001098	0·001827	−0·002018	0·001108
C(3)	0·022312	0·010518	0·001007	−0·004561	−0·002008	0·000373
C(4)	0·018480	0·008073	0·001075	−0·005784	0·001040	−0·000966
C(5)	0·016919	0·005843	0·001081	−0·001756	0·000743	−0·000635
C(6)	0·012945	0·005171	0·000843	0·000210	0·000367	0·000037

(*c*) Isotropic temperature factors for hydrogen in 10^{-16} cm^2.

H(O)	H(2)	H(3)	H(4)	H(5)
7·7	2·7	2·8	3·3	2·3

Table 2. *Comparison between the observed and calculated structure factors*

H	K	L	FOBS	FCAL
0	0	2	574	564
	0	4	1630	1613
	0	6	1790	1742
	0	8	591	610
	0	10	134	104
	0	12	489	559
	0	14	595	573
	0	16	639	627
	0	18	802	854
	0	20	346	348
	0	22	369	368
	0	24	170	174
	0	26	299	310
	0	30	134	135
	0	32	193	189
	0	34	129	115
	0	36	87	93
	0	38	57	53
	0	40	12	20
	0	42	39	40
1	0	0	31	0
2	0	0	783	928
	0	1	30	24
	0	3	1249	1283
	0	4	844	761
	0	5	1374	1374
	0	7	359	400
	0	8	622	599
	0	9	1429	1497
	0	10	336	321
	0	11	279	292
	0	13	673	607
	0	14	502	468
	0	15	612	584
	0	16	253	295
	0	17	514	511
	0	18	222	228
	0	19	159	157
	0	20	102	129
	0	21	288	279
	0	22	304	310
	0	23	351	351
	0	24	346	341
	0	25	82	80
	0	26	91	102
	0	27	264	261
	0	28	17	41
	0	29	75	70
	0	30	183	186
	0	31	57	53
	0	33	132	134
	0	34	42	52
	0	36	90	85
	0	37	26	28
4	0	0	558	463
	0	1	28	26
	0	2	37	15
	0	3	430	394
	0	4	187	166
	0	5	94	91
	0	6	280	246
	0	7	394	374
	0	8	242	229
	0	9	73	59
	0	10	145	146
	0	11	50	56
	0	12	363	350
	0	13	245	238
	0	14	351	361
	0	15	471	488
	0	16	143	148
	0	18	204	181
	0	19	55	90
	0	20	157	187
	0	21	159	163
	0	22	58	66
	0	23	137	130
	0	24	139	146
	0	25	86	90
	0	26	25	22
	0	27	159	165
	0	28	44	59
	0	30	137	148
	0	31	264	264
	0	32	26	63
	0	33	71	72
	0	35	31	35
6	0	0	558	554
	0	7	50	86
	0	9	180	212
	0	10	239	256
	0	11	118	121
	0	12	282	269
	0	13	53	77
	0	15	94	110
	0	16	147	155
	0	18	299	294
	0	19	49	62
	0	22	109	117
	0	23	41	39
	0	24	105	108
	0	25	31	50
	0	27	28	33
	0	28	61	61
	0	29	153	131
	0	30	54	61
8	0	0	228	236
	0	1	187	201
	0	3	125	126
	0	4	79	75
	0	5	185	192
	0	6	84	82
	0	7	20	32
	0	8	61	59
	0	9	227	229
	0	10	66	60
	0	11	68	67
	0	12	69	71
	0	13	109	105
	0	14	79	79
	0	15	136	135
	0	16	86	75
	0	18	191	182
	0	19	85	95
	0	21	159	154
	0	22	27	53
10	0	3	102	112
	0	5	63	53
	0	9	69	77
0	1	2	189	126
	1	4	161	100
	1	6	1158	1181
	1	8	71	112
	1	10	145	92
	1	12	585	582
	1	14	742	770
	1	16	508	481
	1	18	380	379
	1	20	341	348
	1	22	132	146
	1	24	279	274
	1	26	80	93
	1	28	54	52
	1	30	79	77
	1	32	90	87
	1	36	43	51
1	1	1	212	160
	1	2	1519	1737
	1	3	725	831
	1	4	657	769
	1	5	1257	1334
	1	6	203	146
	1	7	387	377
	1	8	395	374
	1	9	54	37
	1	10	677	693
	1	11	929	951
	1	12	409	377
	1	13	192	189
	1	14	448	421
	1	15	110	98
	1	16	279	269
	1	17	259	277
	1	18	157	176
	1	19	145	148
	1	20	451	456
	1	22	257	258
	1	23	386	393
	1	24	159	166
	1	26	181	188
	1	27	121	126
	1	28	256	268
	1	29	59	77
	1	30	104	99
	1	31	57	65
	1	32	137	137
	1	33	15	28
	1	34	79	87
	1	36	48	43
	1	37	102	99
2	1	1	179	155
	1	2	1176	1286
	1	3	145	100
	1	4	278	252
	1	5	429	448
	1	6	83	45
	1	9	155	168
	1	11	140	142
	1	12	194	176
	1	13	79	60
	1	14	303	266
	1	15	71	69
	1	16	234	230
	1	17	247	242
	1	18	154	147
	1	19	105	102
	1	20	103	108
	1	21	75	83
	1	22	199	190
	1	24	55	63
	1	25	76	75
	1	26	42	42
	1	27	140	135
	1	28	53	57
	1	29	66	71
	1	30	139	130
	1	32	55	39
	1	33	53	67
	1	34	56	54
	1	35	59	60
	1	36	12	19
	1	37	48	47
3	1	1	389	400
	1	2	59	60
	1	3	238	206
	1	4	135	120
	1	5	680	650
	1	6	337	290
	1	7	1006	936
	1	8	134	120
	1	9	126	121
	1	10	33	33
	1	11	526	554
	1	12	94	104
	1	13	739	663
	1	14	341	320
	1	15	216	210
	1	16	132	113
	1	17	129	124
	1	19	320	295
	1	19	283	295
	1	20	151	137
	1	21	81	87
	1	23	57	51
	1	24	37	49
	1	25	353	393
	1	26	48	63
	1	27	57	52
	1	28	50	58
	1	29	239	230
	1	30	81	89
	1	31	104	96
	1	32	57	70
	1	34	28	45
	1	35	103	99
	1	36	41	23
4	1	1	17	16
	1	2	70	75
	1	3	391	385
	1	4	119	109
	1	5	41	15
	1	6	156	146
	1	7	491	458
	1	8	95	76
	1	9	75	63
	1	10	150	133
	1	11	278	256
	1	12	150	177
	1	13	239	219
	1	14	85	82
	1	16	170	166
	1	17	150	157
	1	18	70	70
	1	19	104	110
	1	20	57	65
	1	21	159	163
	1	22	44	49
	1	23	36	33
	1	25	84	94
	1	26	43	44
	1	28	55	52
	1	29	94	92
	1	30	10	31
	1	31	26	31
	1	32	24	25
	1	34	42	33
	1	35	22	27
5	1	1	227	198
	1	2	309	321
	1	3	38	60
	1	4	203	260
	1	5	188	232
	1	6	98	103
	1	7	145	141
	1	8	541	519
	1	9	181	172
	1	10	365	328
	1	11	357	329
	1	12	26	25
	1	13	200	183
	1	14	159	186
	1	15	58	59
	1	16	338	333
	1	17	150	148
	1	18	92	99
	1	19	80	69
	1	20	261	235
	1	22	127	115
	1	23	106	120
	1	26	142	136
	1	27	39	55
	1	29	188	163
	1	31	31	25
	1	33	16	37
6	1	1	77	76
	1	2	175	170
	1	3	48	47
	1	4	175	177
	1	5	104	104
	1	6	17	40
	1	7	31	39
	1	8	109	102
	1	9	218	208
	1	10	142	142
	1	11	57	66
	1	12	74	80
	1	13	74	70
	1	14	182	183
	1	16	131	125
	1	17	67	67
	1	18	47	48
	1	20	169	158
	1	21	26	28
	1	26	61	62
	1	29	56	42
	1	31	36	25
7	1	1	280	265
	1	2	219	214
	1	3	41	52
	1	4	137	140
	1	5	74	78
	1	6	230	243
	1	7	61	59
	1	8	80	81
	1	9	77	81
	1	10	165	153
	1	11	97	93
	1	12	16	22
	1	13	65	71
	1	14	153	151
	1	15	66	71
	1	16	123	119
	1	17	178	178
	1	18	94	89
	1	19	43	36
	1	20	146	137
	1	21	68	75
	1	22	57	50
	1	23	75	79
	1	24	96	88
	1	26	87	76
	1	28	85	74
8	1	1	159	153
	1	2	52	64
	1	3	69	71
	1	4	49	54
	1	5	73	75
	1	7	61	67
	1	8	20	34
	1	9	48	44
	1	12	34	21
	1	15	89	73
	1	16	49	37
	1	17	34	21
	1	20	15	29
	1	21	34	31
	1	23	92	87
9	1	1	101	94
	1	2	50	53
	1	4	66	61
	1	5	101	103
	1	7	134	130
	1	9	46	31
	1	11	109	90
	1	12	95	86
	1	13	53	51
	1	15	39	49
	1	18	17	9
	1	19	81	75
10	1	6	39	24
	1	10	56	29
0	2	0	1465	1316
	2	2	318	292
	2	4	22	22
	2	6	733	784
	2	8	715	758
	2	10	151	149
	2	12	618	617
	2	14	382	357
	2	18	489	501
	2	20	73	73
	2	24	177	187
	2	26	317	324
	2	28	169	174
	2	30	120	130
	2	32	91	87
	2	34	110	115
	2	36	40	36
1	2	0	1170	1348
	2	1	269	251
	2	2	263	140
	2	3	1372	1494
	2	4	511	450
	2	5	378	337
	2	6	349	349
	2	7	604	561
	2	8	555	539
	2	9	905	928
	2	10	23	19
	2	11	26	12
	2	12	159	162
	2	13	239	212
	2	14	30	42
	2	15	89	86
	2	16	177	157
	2	17	117	105
	2	18	121	122
	2	19	140	134
	2	20	25	35
	2	21	210	209
	2	22	450	463
	2	23	131	140
	2	24	264	271
	2	25	34	34
	2	27	83	76
	2	30	147	149
	2	31	75	77
	2	32	102	103
	2	34	27	23
	2	36	53	44
2	2	0	408	357
	2	1	594	686
	2	2	624	651
	2	3	417	463
	2	4	682	722
	2	5	638	626
	2	6	328	325
	2	7	395	411
	2	8	370	325
	2	9	700	731
	2	10	62	40
	2	11	84	94
	2	12	91	76
	2	13	138	121
	2	14	191	189
	2	15	294	286
	2	16	83	97
	2	17	283	277
	2	18	276	270
	2	19	29	21
	2	20	52	56
	2	21	359	351
	2	22	236	248
	2	23	119	109
	2	24	108	102
	2	25	134	129
	2	26	93	98
	2	27	156	155
	2	28	52	52
	2	30	74	71
	2	31	39	26
	2	33	75	77
	2	35	55	52
	2	36	101	98
	2	37	53	56
3	2	0	290	259
	2	1	554	515
	2	2	132	138
	2	4	279	229
	2	5	28	27
	2	6	157	142
	2	7	454	436
	2	8	105	93
	2	9	343	319
	2	10	353	311
	2	11	308	291
	2	12	10	20
	2	13	104	113
	2	14	195	155
	2	15	254	277
	2	16	54	41
	2	17	102	108
	2	18	39	27
	2	19	112	126
	2	20	47	76
	2	21	176	183
	2	22	58	79
	2	23	37	12
	2	24	85	93
	2	25	207	219
	2	26	58	78
	2	27	249	253
	2	28	27	49
	2	29	53	52
	2	30	48	55
	2	31	110	107
	2	32	85	93
	2	33	89	104
	2	35	31	22
	2	36	46	50
4	2	0	328	354
	2	1	103	111
	2	2	314	314
	2	3	322	303
	2	4	454	474
	2	5	125	132
	2	6	206	204
	2	7	81	79
	2	8	103	105
	2	9	392	397
	2	10	76	82
	2	11	238	236
	2	12	272	279
	2	13	398	411
	2	14	118	122
	2	15	219	221
	2	16	45	43
	2	17	90	98
	2	18	193	188
	2	19	56	50
	2	20	53	55
	2	21	57	87
	2	22	73	57
	2	23	97	109
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Table 2 (*cont.*)

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	4	6	405	406
	4	7	300	288
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	4	21	48	46
	4	22	229	228
	4	23	38	43
	4	24	233	230
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	4	27	109	114
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	4	7	50	40
	4	8	49	42
	4	9	200	160
	4	10	535	475
	4	11	142	134
	4	12	399	388
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	4	15	210	211
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	7	3	47	49
	7	4	70	82
	7	5	64	64
	7	6	155	166
	7	7	183	233
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	7	9	73	82
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	7	17	49	54
	7	18	120	113
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	7	23	55	49
	7	24	45	39
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	7	12	49	52
	7	13	60	59
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	7	20	118	103
	7	22	62	62
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	7	6	67	33
	7	7	75	78
	7	8	46	45
	7	10	46	42
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Table 2 (*cont.*)

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	8	14	299	318
	8	16	211	224
	8	18	274	294
	8	20	75	72
	8	22	221	225
	8	24	145	153
	8	26	81	85
	8	28	133	132
	8	30	155	162
	8	32	65	64
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	8	7	59	66
	8	8	81	83
	8	9	35	12
	8	10	147	139
	8	11	29	41
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	8	13	17	10
	8	14	17	10
	8	16	37	39
	8	17	32	15
	8	18	33	22
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	8	27	57	58
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	11	5	77	77
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	11	24	18	32
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	15	8	18	26
	15	9	16	2
7	15	1	128	125
	15	4	24	29

negligible. The weighting scheme used in the refinement was; $w=1\cdot0$ for $|F_{obs}|\leq 40$, $w=40\cdot0/|F_{obs}|$ for $|F_{obs}|\geq 40$ and unobserved reflections were given zero weight. The atomic scattering factors used in the structure-factor calculations were taken from *International Tables for X-ray Crystallography* (1962). The atomic coordinates, their standard deviations and thermal parameters at this stage are listed in Table 1. The observed and calculated structure factors are compared in Table 2.

Discussion

The crystal structure of ammonium acid *o*-carboxybenzenesulfonate is ionic, consisting of ammonium ions and acid *o*-carboxybenzenesulfonate ions; as expected, the latter possess the formula $C_6H_4.COOH.SO_3^-$, with an ionized sulfonate and an un-ionized carboxyl group. The structure of the *o*-carboxybenzenesulfonate as a whole is isomorphous and isostructural with the ammonium acid phthalate structure, the sulfonate groups replacing the ionized carboxyl groups of the acid phthalate ions, $C_6H_4COOHCOO^-$, in the latter structure; also, as in the phthalate structures, one finds a short hydrogen bond of $2\cdot64_0$ Å from O(I) of the carboxyl group of one ion to O(3) of the sulfonate group of another ion related to the first by the *a*-glide perpendicular to the *b* axis. The pertinent data for this hydrogen bond are: O(I)–H, 1·0 Å; H···O(3), 1·7 Å and O(I)–H···O(3), 156°. The ammonium ion is surrounded by eight oxygen atoms: three O(1) at distances $2\cdot88_9$, $2\cdot94_3$ and $3\cdot02_0$ Å, two O(2) at $3\cdot24_7$ and $2\cdot87_7$ Å; one O(3) at $3\cdot05_2$ Å and finally two O(I′) at $3\cdot04_6$ and $2\cdot98_0$ Å, thus drawing six neighbors from sulfonate groups (Table 3). It is obvious that O(I), which retains its proton, is not involved in an NH_4-O contact. These NH_4-O contacts and the mode of coordination are quite normal as compared with other ammonium salts. A schematic drawing of a part of the unit cell viewed down the *a* axis is shown in Fig. 1. As in the acid phthalate structures, the aromatic *o*-carboxybenzenesulfonate ions make infinite chains along the *a* axis by the hydrogen bonds; these chains are arranged around the cations which are situated near the plane $z=0$. The sandwich-like sheets thus formed perpendicular to the *c* axis stack in the structure by the aromatic van der Waals contact around the two-fold screw axes on the planes $z=\frac{1}{4}$. The structure accounts for the perfect cleavage perpendicular to the *c* axis. In the potassium acid phthalate structure, all the infinite chains of acid phthalate ions have the same polarity, whereas in the present crystal the infinite chains of one polarity are related to those of inverse polarity by the centers of symmetry.

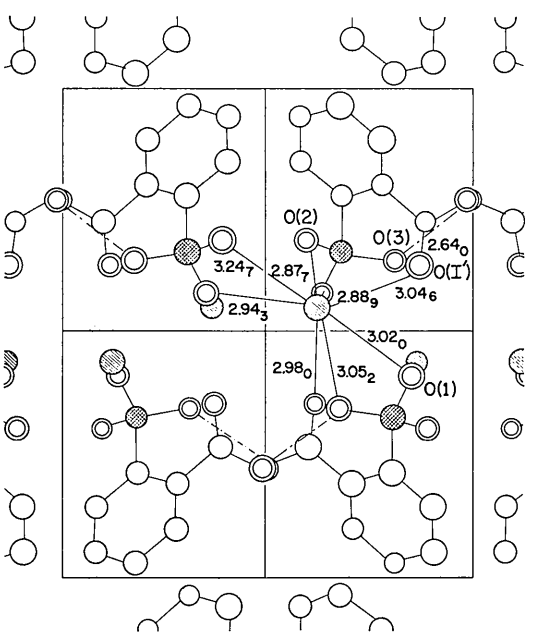

Fig. 1. A schematic drawing of part of the unit cell viewed down the *a* axis. The short O(I)–H···O(3) bonds are shown by chain lines.

Table 3. *Coordination around the ammonium ion*

Contacts	Distances	With	At
1	2·943	O(1)	$(\frac{1}{2}+x, \frac{1}{2}-y, z)$
2	2·889	O(1)	(x, y, z)
3	3·020	O(1)	$(1-x, -y, -z)$
4	3·052	O(3)	$(1-x, -y, -z)$
5	2·877	O(2)	$(1+x, y, z)$
6	3·247	O(2)	$(\frac{1}{2}+x, \frac{1}{2}-y, z)$
7	2·980	O(I′)	$(1-x, -y, -z)$
8	3·046	O(I′)	(x, y, z)

Bond distances and angles in the *o*-carboxybenzenesulfonate ion are shown in Figs. 2 and 3. The unionized carboxyl group has, as usual, two unequal C–O distances and also unequal C–C–O angles; these values agree quite well with those in the potassium acid phthalate structure which exhibits C=O, $1\cdot20_1$; C–O, $1\cdot30_5$; C–C, $1\cdot49_8$ Å. The data on the planarity of the group are shown in Fig. 4. The S–O distances of $1\cdot43_6$, $1\cdot44_4$ and $1\cdot45_3$ Å are normal for an aromatic sulfonate group; as discussed above O(1) is involved in three NH_4–O contacts, O(3) in one contact and a hydrogen bond, whereas one of the two contacts made by O(2) is relatively long. The slight shortening of the S–O(2) distance when compared with the other two might indicate an effect of the unequal surroundings of the three oxygen atoms. The average O–S–O and C–S–O angles in the group are 112·4° and 106·4°, respectively; these deviations from the normal tetrahedral angle in sulfonate groups have been established by many accurate structure analyses; *e.g.* 112·9° and 106·7° in the structure of taurine, 2-aminoethylsulfonic acid (Okaya, 1966), 113° and 106° in 2-diazo-4-phenolsulfonate monohydrate, $C_6H_3(N\equiv N)^+OH(SO_3)^-.H_2O$ (Greenberg & Okaya, 1967), and others.

The benzene ring is a slightly distorted regular hexagon and the average of C–C distances (excluding the shortest C(3)–C(4) distance) is $1\cdot38_7$ Å; the deviation of the C(3)–C(4) distance from this average might be significant. There is no such deviation in the angles

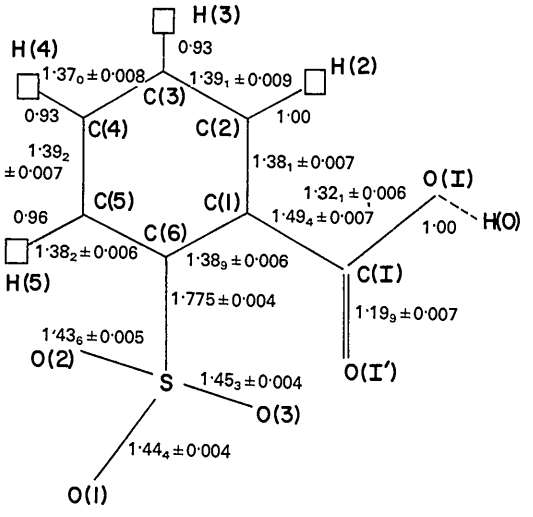

Fig. 2. Bond distances in the *o*-carboxybenzenesulfonate ion.

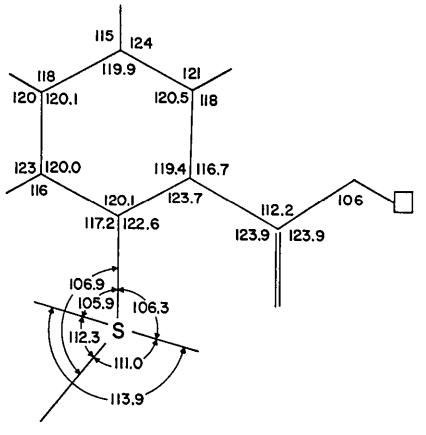

Fig. 3. Bond angles.

in the hexagon from the average of 120·0°. The equation of the ring plane is calculated in the usual manner and the deviations of the ring atoms, as well as C(I) and S from the plane are shown in Fig. 5. The average C–H distance of 0·95 Å is again quite normal for that obtained by the X-ray method.

Owing to steric hindrance, the carboxyl group can no longer stay in the plane of benzene ring and makes an angle of 50·7°. This value is to be compared with that of 31·7° between the un-ionized carboxyl group and the benzene ring in the potassium acid phthalate structure; the effect of the hindrance due to the larger size of the sulfonate group is demonstrated. Steric hindrance also affects the angles around C(1) and C(6)

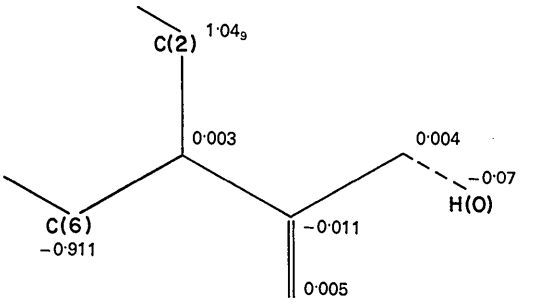

Fig. 4. The planarity of the carboxyl group. The least-squares plane is: $0{\cdot}0157X+0{\cdot}9538Y+0{\cdot}3001Z=4{\cdot}1062$. ($X$, Y, and Z measured in Å).

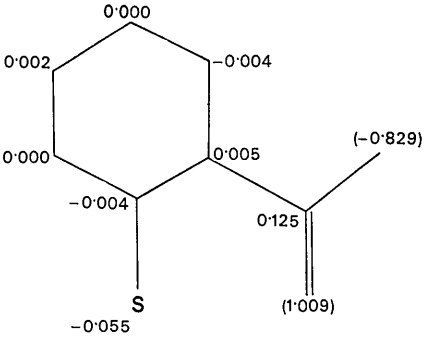

Fig. 5. Deviations of atoms from the benzene ring plane. C(I) and S were excluded from the evaluation of the least-squares plane: $0{\cdot}4950X+0{\cdot}7299Y-0{\cdot}4712Z=0{\cdot}2231$.

(Fig. 3) and displaces C(I) and S from the ring plane by +0·125 and −0·055 Å respectively (Fig. 5).

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