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Hydrogen Bond Studies. LIII.* The Crystal Structure of 2,5-Dichlorobenzenesulphonic Acid Trihydrate, $H_7O_3^+C_6H_3Cl_2SO_3^-$

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The crystal structure of 2,5-dichlorobenzenesulphonic acid trihydrate has been determined from three-dimensional single-crystal X-ray diffraction data recorded on a Stoe–Philips two-circle Weissenberg diffractometer at room temperature. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a cell of dimensions $a=7{\cdot}350$, $b=23{\cdot}516$, $c=6{\cdot}862$ Å, $\beta=100{\cdot}68°$. The structure comprises oxonium ions tightly bonded to two water molecules to form $H_7O_3^+$ ions. Very large anisotropy in the thermal parameters of the oxygen atoms indicates some form of disorder, which makes the determination of the geometry of the $H_7O_3^+$ ion less precise. O–H···O distances in the ion, as obtained from least-squares refinements using an ordered model, are 2·37 (1) and 2·42 (1) Å. The $H_7O_3^+$ ions and 2,5-dichlorobenzenesulphonate ions are hydrogen bonded together to form layers. No hydrogen bonds exist between individual $H_7O_3^+$ ions.

Introduction

This work is part of the systematic studies of the solid hydrates of strong acids currently in progress at this Institute. References to earlier works can be found in a paper by Lundgren (1972). The structure determination of 2,5-dichlorobenzenesulphonic acid trihydrate reported in the present paper is based on single-crystal X-ray diffraction data collected at room temperature.

Crystal data

2,5-Dichlorobenzenesulphonic acid trihydrate, $C_6H_3Cl_2SO_3H.3H_2O$; F.W. 281·11; monoclinic, $a=7{\cdot}350$ (2),† $b=23{\cdot}516$ (3), $c=6{\cdot}862$ (1) Å, $\beta=100{\cdot}68$ (4)°, $V=1165{\cdot}5$ Å^3 at 22°C; $Z=4$, $D_x=1{\cdot}602$ g.cm^{-3}; space group $P2_1/c$.

Experimental

2,5-Dichlorobenzenesulphonic acid was made from *p*-dichlorobenzene and fuming sulphuric acid following a method described by de Crauw (1931). The trihydrate was crystallized from an aqueous solution of the acid. Crystals of suitable dimensions were cut from the resulting large flat needle-shaped crystals and mounted in thin-walled glass capillaries with four crystal faces parallel to the capillary axis. Crystals which are not protected in this way will lose some of their water to the atmosphere within a few hours.

The intensity data were recorded at room temperature using a crystal of dimensions $0{\cdot}17 \times 0{\cdot}13 \times 0{\cdot}32$ mm. The measurements were made on a Stoe–Philips automated two-circle X-ray diffractometer using Cu $K\alpha$ radiation and an ω–2θ scan technique (*cf.* Lundgren, 1972). Seven layers $0 \le l \le 6$ were recorded, giving a total of 2023 independent reflexions. This corresponds to about 70% of the reflexions within the copper reflexion sphere. 681 reflexions with $I < 2\sigma(I)$, where $\sigma(I)$ is based on counting statistics, were considered to be insignificantly different from the background and were given zero weight in the refinements. The intensity of the 002 reflexion was very high and therefore considered to be less accurately measured. The reflexion was used only when the structure was solved and was given zero weight in other calculations.

The data were corrected for the Lorentz, polarization, absorption and secondary extinction effects. The linear absorption coefficient for Cu $K\alpha$ radiation is 67·09 cm^{-1}. The absorption correction was made using the program *DATAP*2, written by Coppens, Leiserowitz & Rabinovich (1965). The minimum and maximum values of the transmission factors were 0·3511 and 0·4920.

The cell dimensions were determined from quartz-calibrated oscillation photographs taken in a Weissenberg camera with Cu $K\alpha$ radiation at room temperature [$\lambda(\text{Cu } K\alpha_1)=1{\cdot}54051$, $\lambda(\text{Cu } K\alpha_2)=1{\cdot}54433$ Å, $a_{SiO_2}=4{\cdot}9131$ Å]. The cell parameters were fitted to the measured θ values by least-squares methods using the program *CELSIUS*. This and other programs mentioned in the following are described briefly by Liminga (1967).

Space group and structure determination

The intensity data indicated uniquely the space group $P2_1/c$ (No. 14, *International Tables for X-ray Crystallography*, 1952).

The coordinates of the chlorine and sulphur atoms were determined from a three-dimensional Patterson synthesis and the positions of the other heavy atoms

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† Numbers in parenthesis here and throughout this paper are the estimated standard deviations in the least significant digits.

were derived from subsequent electron-density calculations. All atoms occupy the general fourfold positions of $P2_1/c$.

The atomic coordinates were improved in a series of electron-density calculations using the program *DRF*. The scale factor, atomic coordinates and individual isotropic thermal parameters were thereafter refined in a series of least-squares calculations. The refinement ceased to converge at an R value of 0·17 (0·23). The discrepancy index is defined as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| .$$

(zero-weight data not included). The R value including zero-weight data is given in parenthesis.

On introducing anisotropic thermal parameters into the refinement the R value decreased to 0·073 (0·119). The number of parameters in the anisotropic refinement was 136 compared with 61 in the isotropic refinement. A difference Fourier synthesis calculated at this stage showed three well-resolved peaks corresponding to the hydrogen atoms bonded to the carbon ring. Four of the hydrogen atoms (those of the water molecules) could also be located, but these were more diffuse. An anisotropic least-squares refinement with these seven hydrogen atoms included with fixed parameters lowered R to 0·066. The hydrogen atoms were given a Debye–Waller factor of $B = 5·0$ Å^2.

Extinction correction was then applied according to the formula given by Zachariasen (1963). The constant in the formula was determined from the 20 strongest reflexions. The subsequent anisotropic refinement gave the final R values 0·064 (0·109). In the last cycle the shifts on the parameters were less than one tenth of the estimated standard deviations.

The thermal ellipsoids of some of the oxygen atoms indicated very strong anisotropy, and one O···O hydrogen bond distance was very short (2·37 Å). Attempts were therefore made to refine a model including two half oxygen atoms for O(*W*2), which showed the largest anisotropy. The calculations showed, however, that if

Table 1. *Atomic coordinates* ($\times 10^5$)

Atom	x	y	z
Cl(1)	14216 (24)	36370 (10)	18863 (35)
Cl(2)	79514 (34)	19261 (9)	27590 (31)
S	56662 (21)	40997 (6)	24956 (23)
O(1)	76657 (58)	41309 (19)	27727 (73)
O(2)	48101 (99)	43421 (24)	6482 (86)
O(3)	49769 (71)	43330 (22)	41232 (90)
C(1)	50906 (77)	33666 (25)	23619 (79)
C(2)	32646 (82)	31757 (29)	20798 (91)
C(3)	29241 (96)	25980 (34)	19988 (98)
C(4)	43451 (124)	22135 (28)	21696 (96)
C(5)	61539 (104)	24086 (28)	24926 (87)
C(6)	65431 (81)	29810 (24)	25520 (82)
O(*W*1)	28425 (68)	7342 (30)	19114 (70)
O(*W*2)	95243 (76)	5940 (41)	12573 (89)
O(*W*3)	79271 (87)	2249 (28)	36707 (102)
H(3)	15200	24500	17700
H(4)	40500	17700	21000
H(6)	79500	31300	27800

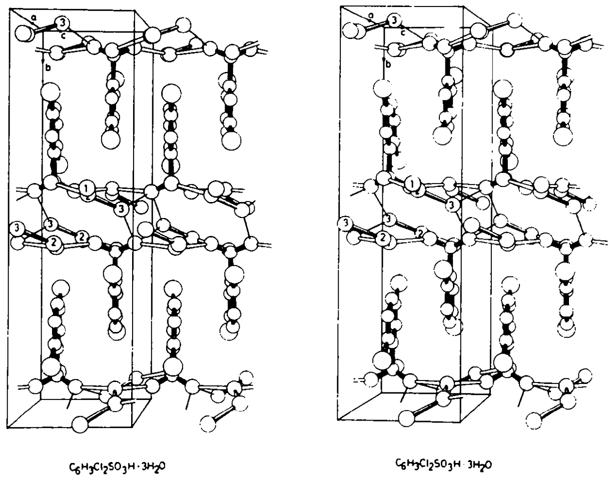

Fig. 1. Stereoscopic drawing of the crystal structure of $H_7O_3^+C_6H_3Cl_2SO_3^-$. The structure is viewed along the a axis. The oxygen atoms of the $H_7O_3^+$ ion are denoted by 1, 2 and 3. Covalent bonds are filled. Hydrogen bonds within $H_7O_3^+$ are half filled and other hydrogen bonds are open. Other short contacts are represented by a single line.

Table 2. *Anisotropic thermal parameters* ($\times 10^4$)

The form of the temperature factor is $\exp[-(\beta_{11}h^2 + \cdots + 2\beta_{12}hk + \cdots)]$. The r.m.s. components (R_i) of thermal displacement of the atoms along the ellipsoid axes are also listed ($\times 10^3$ Å).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Cl(1)	157 (3)	40 (1)	552 (8)	1 (1)	4 (5)	−34 (2)	222 (4)	297 (3)	379 (4)
Cl(2)	472 (7)	24 (1)	377 (6)	42 (2)	55 (6)	8 (1)	202 (2)	304 (4)	390 (4)
S	185 (3)	18 (1)	268 (4)	0 (1)	0 (4)	−4 (1)	211 (3)	224 (2)	265 (3)
O(1)	187 (9)	24 (1)	469 (15)	−16 (4)	95 (13)	−21 (4)	203 (9)	256 (10)	338 (8)
O(2)	603 (23)	30 (1)	464 (18)	−36 (6)	−257 (24)	50 (6)	217 (13)	276 (12)	511 (15)
O(3)	297 (13)	30 (1)	645 (21)	−18 (4)	224 (19)	−72 (6)	208 (14)	256 (11)	433 (11)
C(1)	355 (11)	20 (1)	225 (14)	6 (4)	27 (14)	3 (4)	205 (12)	227 (11)	242 (12)
C(2)	219 (13)	19 (2)	220 (16)	−1 (5)	33 (16)	−2 (6)	212 (13)	248 (14)	286 (12)
C(3)	189 (16)	20 (2)	202 (18)	−2 (6)	23 (19)	−8 (6)	215 (16)	256 (14)	325 (16)
C(4)	188 (24)	27 (1)	266 (16)	−10 (7)	24 (21)	−14 (5)	211 (15)	235 (15)	355 (12)
C(5)	261 (20)	28 (1)	309 (15)	−30 (6)	71 (19)	−22 (5)	224 (12)	240 (12)	312 (10)
C(6)	459 (12)	20 (1)	218 (14)	−21 (4)	71 (14)	−9 (4)	222 (12)	234 (11)	243 (9)
O(*W*1)	246 (12)	64 (2)	265 (13)	−15 (6)	31 (13)	8 (6)	243 (9)	257 (11)	425 (8)
O(*W*2)	200 (12)	110 (4)	403 (18)	13 (8)	19 (16)	68 (9)	226 (9)	292 (11)	563 (12)
O(*W*3)	369 (17)	42 (2)	629 (24)	0 (6)	202 (24)	26 (7)	275 (13)	336 (12)	401 (12)

the anisotropy does indicate disorder, then it is too small to be detected using the present data.

The least-squares refinements were performed with the full-matrix program *LALS*, where the quantity $\sum w(|F_o|-|F_c|)^2$ is minimized. The weights were calculated according to the expression $w=1/(a+|F_o|+c|F_o|^2)$. The final values used for the parameters a and c were 20·0 and 0·016 respectively. A weight analysis showed that these values were satisfactory. The atomic scattering factors used were those for neutral Cl, S, O and C given in the *International Tables for X-ray Crystallography* (1962). The spherical scattering factor used

Table 3. *Observed and calculated structure factors*

The columns are in the order h, k, $10|F_o|$, $10|F_c|$. Reflexions marked * were given zero weights in the refinements.

h	k	$10\vert F_o\vert$	$10\vert F_c\vert$
H,K,0			
1	0	1051	1099
2	0	265	280
3	0	775	731
4	0	179	168
5	0	33	12*
6	0	74	60
7	0	146	137
8	0	36	16*
1	1	238	213
2	1	166	161
3	1	10	53*
4	1	293	296
5	1	288	292
6	1	234	251
7	1	00	03*
8	1	81	90
0	2	86	157
1	2	114	70*
2	2	512	473
3	2	247	179
4	2	339	317
5	2	22	11*
6	2	143	130
7	2	25	22*
8	2	00	33*
1	3	00	50*
2	3	295	311
3	3	222	209
4	3	148	148
5	3	477	464
6	3	00	27*
7	3	32	31*
8	3	29	27*
0	4	338	355
1	4	43	48
2	4	270	279
3	4	481	450
4	4	81	95
5	4	75	69
6	4	20	09*
7	4	171	168
8	4	44	41
1	5	378	380
2	5	512	478
3	5	377	361
4	5	155	134
5	5	157	155
6	5	00	02*
7	5	50	00*
8	5	67	63
0	6	872	840
1	6	852	897
2	6	509	502
3	6	171	172
4	6	200	195
5	6	29	27*
6	6	265	233
7	6	105	96
8	6	80	78
1	7	404	420
2	7	617	617
3	7	384	382
4	7	69	74
5	7	129	117
6	7	75	58
7	7	19	09*
8	7	19	16*
0	8	953	882
1	8	510	546
2	8	116	95
3	8	00	10*
4	8	409	423
5	8	09	11*
6	8	22	17*
7	8	125	145
8	8	68	55
1	9	731	708
2	9	304	304
3	9	148	152
4	9	413	401
5	9	17	34*
6	9	106	106
7	9	24	14*
8	9	36	43
0	10	239	255
1	10	111	103
2	10	325	302
3	10	18	22*
4	10	56	63
5	10	261	254
6	10	118	126
7	10	23	25*
8	10	98	91
1	11	454	452
2	11	104	84
3	11	201	202
4	11	06	35*
5	11	81	73
6	11	00	08*
7	11	53	37
8	11	00	06*
0	12	409	386
1	12	533	532
2	12	163	158
3	12	78	56
4	12	218	230
5	12	00	04*
6	12	156	142
7	12	30	15*
1	13	350	351
2	13	42	04*
3	13	231	196
4	13	354	365
5	13	118	126
6	13	115	102
7	13	20	27*
0	14	182	187
1	14	54	40
2	14	192	196
3	14	212	200
4	14	67	48
5	14	60	72
6	14	61	55
7	14	55	53
1	15	15	56*
2	15	180	172
3	15	123	107
4	15	66	62
5	15	90	81
6	15	00	59*
7	15	44	34
0	16	87	100
1	16	136	149
2	16	188	194
3	16	00	15*
4	16	00	07*
5	16	78	66
6	16	125	117
7	16	43	50
1	17	85	86
2	17	00	03*
3	17	105	107
4	17	56	73
5	17	72	67
6	17	100	103
7	17	03	17*
0	18	443	412
1	18	73	52
2	18	199	217
3	18	80	92
4	18	76	66
5	18	110	105
6	18	36	21*
1	19	214	224
2	19	133	144
3	19	83	83
4	19	165	175
5	19	102	99
6	19	28	14*
0	20	35	51*
1	20	10	26*
2	20	41	34*
3	20	30	11*
4	20	12	59*
5	20	62	56
6	20	00	14*
1	21	21	42*
2	21	85	78
3	21	45	02*
4	21	34	40*
5	21	137	127
0	22	138	116
1	22	13	30*
2	22	32	19*
3	22	07	17*
4	22	00	18*
5	22	19	61*
1	23	00	04*
2	23	28	09*
3	23	45	36
4	23	32	32*
5	23	40	64
0	24	19	02*
1	24	51	48
2	24	52	60
3	24	24	15*
4	24	00	26*
1	25	00	02*
2	25	104	102
3	25	85	92
4	25	39	32
0	26	18	17*
1	26	65	43
2	26	60	67
3	26	00	00*
1	27	79	80
2	27	24	08*
0	28	99	101
1	28	39	41
H,K,1			
-8	1	22	45*
-7	1	87	84
-6	1	94	97
-5	1	233	222
-4	1	30	54*
-3	1	243	252
-2	1	600	621
-1	1	24	67*
0	1	86	142
1	1	132	98
2	1	991	1004
3	1	228	219
4	1	201	205
5	1	340	314
6	1	43	23*
7	1	31	12*
8	1	30	21*
-8	2	26	03*
-7	2	145	141
-6	2	51	75
-5	2	31	26*
-4	2	203	217
-3	2	680	677
-2	2	240	251
-1	2	769	726
0	2	906	1001
1	2	542	510
2	2	581	592
3	2	286	288
4	2	205	206
5	2	88	104
6	2	08	19*
7	2	163	172
8	2	50	45
-8	3	93	82
-7	3	47	22
-6	3	00	50*
-5	3	322	304
-4	3	119	101
-3	3	191	174
-2	3	571	580
-1	3	691	688
0	3	195	166
1	3	382	399
2	3	418	421
3	3	160	157
4	3	39	07*
5	3	186	159
6	3	128	123
7	3	24	38*
8	3	33	45*
-8	4	47	46
-7	4	24	19*
-6	4	249	273
-5	4	237	230
-4	4	178	181
-3	4	783	761
-2	4	88	100
-1	4	384	335
0	4	305	328
1	4	539	517
2	4	222	227
3	4	406	402
4	4	129	127
5	4	367	373
6	4	141	149
7	4	66	48
8	4	57	56
-8	5	00	33*
-7	5	00	41*
-6	5	00	24*
-5	5	307	323
-4	5	200	199
-3	5	328	326
-2	5	319	352
-1	5	987	980
0	5	306	288
1	5	847	870
2	5	39	25
3	5	259	273
4	5	409	413
5	5	259	263
6	5	22	13*
7	5	55	39
8	5	29	06*
-8	6	17	06*
-7	6	126	122
-6	6	46	30
-5	6	238	241
-4	6	46	41
-3	6	424	430
-2	6	390	405
-1	6	157	143
0	6	988	988
1	6	633	650
2	6	00	45*
3	6	562	540
4	6	226	219
5	6	53	41
6	6	24	47*
7	6	101	101
8	6	30	27*
-8	7	66	72
-7	7	39	18*
-6	7	123	134
-5	7	71	66
-4	7	177	174
-3	7	54	55
-2	7	141	135
-1	7	754	720
0	7	384	361
1	7	411	422
2	7	99	85
3	7	223	229
4	7	156	156
5	7	37	00*
6	7	217	209
7	7	48	48
8	7	31	29*
-8	8	56	65
-7	8	00	17*
-6	8	251	239
-5	8	115	124
-4	8	151	171
-3	8	247	220
-2	8	78	73
-1	8	280	279
0	8	131	123
1	8	196	192
2	8	75	60
3	8	81	24*
4	8	101	99
5	8	173	178
6	8	174	170
7	8	39	18*
8	8	89	98
-8	9	53	33
-4	9	91	84
-7	9	26	21*
-6	9	57	03*
-5	9	134	132
-3	9	174	174
-2	9	167	167
-1	9	24	61*
0	9	89	92
1	9	236	207
2	9	171	179
3	9	152	133
4	9	78	62
5	9	86	86
6	9	34	27*
7	9	41	29*
8	9	18	18*
-8	10	24	23*
-7	10	49	64
-6	10	122	116
-5	10	33	19*
-4	10	129	132
-3	10	84	76
-2	10	401	397
-1	10	606	574
0	10	266	264
1	10	591	572
2	10	297	295
3	10	84	71
4	10	75	81
5	10	116	106
6	10	19	18*
7	10	38	28*
-8	11	80	85
-7	11	26	14*
-6	11	154	144
-5	11	46	47*
-4	11	235	238
-3	11	217	242
-2	11	100	106
-1	11	307	305
0	11	56	69
1	11	217	237
2	11	00	06*
3	11	338	361
4	11	161	165
5	11	97	75
6	11	164	162
7	11	48	52
-8	12	48	53
-7	12	37	10*
-6	12	82	74
-5	12	33	17*
-4	12	144	139
-3	12	379	358
-2	12	328	330
-1	12	176	168
0	12	167	174
1	12	398	390
2	12	110	120
3	12	322	327
4	12	17	28*
5	12	14	24*
6	12	62	71
7	12	25	01*
-7	13	00	06*
-6	13	47	20*
-5	13	123	141
-4	13	175	172
-3	13	121	110
-2	13	40	45
-1	13	330	339
0	13	77	94
1	13	321	327
2	13	60	50
3	13	69	58
4	13	203	195
5	13	109	117
6	13	17	03*
7	13	32	23*
-7	14	00	28*
-6	14	130	124
-5	14	86	75
-4	14	152	170
-3	14	145	127
-2	14	13	10*
-1	14	83	69
0	14	291	293
1	14	142	131
2	14	52	40
3	14	236	228
4	14	190	191
5	14	125	116
6	14	85	93
7	14	00	22*
-7	15	47	51
-6	15	12	42*
-5	15	38	52*
-4	15	342	345
-3	15	79	79
-2	15	185	189
-1	15	228	216
0	15	45	46
1	15	136	136
2	15	183	191
3	15	177	198
4	15	219	213
5	15	00	01*
6	15	46	53
7	15	27	07*
-7	16	74	51
-6	16	24	26*
-5	16	51	44
-4	16	131	112
-3	16	00	12*
-2	16	59	54
-1	16	54	40
0	16	108	108
1	16	113	94
2	16	91	86
3	16	41	46*
4	16	110	120
5	16	00	09*
6	16	63	49
7	16	29	39*
-7	17	00	01*
-6	17	66	37
-5	17	132	141
-4	17	39	44*
-3	17	105	109
-2	17	303	308
-1	17	176	155
0	17	00	02*
1	17	193	199
2	17	300	282
3	17	28	54*
4	17	79	62
5	17	143	149
6	17	28	18*
-6	18	85	95
-5	18	42	75*
-4	18	26	19*
-3	18	44	22*
-2	18	57	17*
-1	18	110	117
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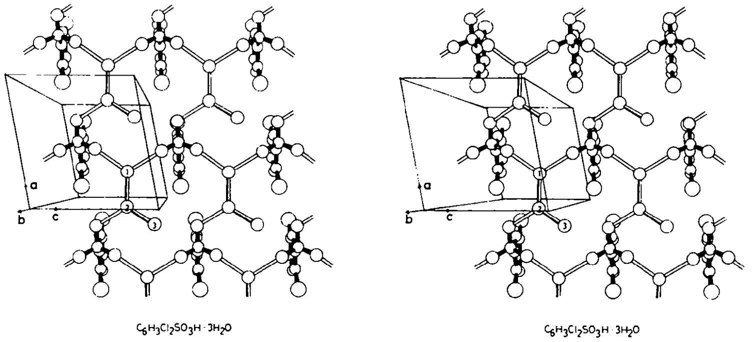

Fig. 2. Stereoscopic drawing showing the structure viewed along the *b* axis. For notation see Fig. 1.

for the hydrogen atoms was that proposed by Stewart, Davidson & Simpson (1965). All calculations were performed on the CDC 3600 computer in Uppsala.

The atomic parameters from the final refinement are listed in Tables 1 and 2. The root-mean-square components of thermal displacement along the principal axes of vibration are given in Table 2. Observed and calculated structure factors are compared in Table 3.

Description of the structure

The structure is illustrated in Figs. 1, 2 and 3. Bond distances and angles are shown in Figs. 4 and 5. The bond distances are also listed in Table 4. Interatomic distances and angles have been calculated with the program *ORFFE*. Standard deviations have been estimated from the errors in the atomic coordinates obtained in the form of a variance–covariance matrix from the final cycle of refinement. The effect of uncertainties in the cell dimensions have also been taken into account. All illustrations in this paper have been prepared with the plotting program *ORTEP*.

It was not possible to locate all hydrogen atoms experimentally in this investigation. The hydrogen bonds have therefore been derived from those hydrogen atom positions obtained in combination with heavy atom interatomic distance and angle considerations.

The structure is made up of both oxonium ions tightly bonded to two water molecules and of 2,5-dichlorobenzenesulphonate ions. The oxonium ions, water molecules and sulphonate groups are hydrogen bonded together to form layers parallel to the *ac* plane. These layers face one another in pairs. The carbon rings point outwards from these layers; in the positive **b** direction from one layer and in the negative **b** direction from the other (see Fig. 1). A short contact between two facing layers occurs between O(*W*3) and an oxygen atom of the sulphonate group, in which the distance is 2·99 Å. This is possibly a weak hydrogen bond. The shortest distance between two atoms in carbon rings belonging to different layers is 3·46 Å. The angle between the planes of these rings is 1·8°; the angle between the plane of a carbon ring and the *ab* plane is 8·0°.

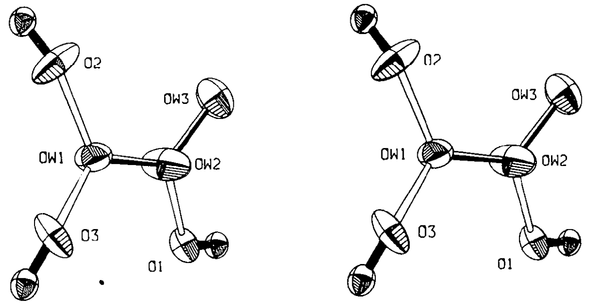

Fig. 3. The hydrogen bond system around the $H_7O_3^+$ ion. The ellipsoids are scaled to enclose 50% probability. For notation see Fig. 1.

Table 4. *Interatomic distances*

Distances corrected for thermal riding motion are given within brackets.

(*a*) Covalent bonds

C(1)–C(2)	1·394 (8) Å	C(2)–Cl(1)	1·721 [1·750] (7) Å
C(2)–C(3)	1·381 (10)	C(5)–Cl(2)	1·725 [1·750] (8)
C(3)–C(4)	1·370 (11)	C(1)–S	1·773 (6)
C(4)–C(5)	1·385 (11)	S----O(1)	1·448 [1·469] (5)
C(5)–C(6)	1·375 (9)	S----O(2)	1·426 [1·504] (5)
C(6)–C(1)	1·388 (8)	S----O(3)	1·419 [1·466] (5)
C(3)–H(3)	0·98		
C(4)–H(4)	0·89		
C(6)–H(6)	0·89		

(*b*) Hydrogen bonds

O(*W*1)···O(2)	2·706 (8) Å
···O(3)	2·694 (7)
O(*W*2)···O(1)	2·606 (8)
···O(*W*1)	2·419 (8)
···O(*W*3)	2·366 (9)

In Fig. 2 a hydrogen bonded layer is viewed along its planar normal.

Hydrogen bonds. $H_7O_3^+$

There are seven hydrogen atoms available for hydrogen bonding in the asymmetric unit. The interatomic distances and angles indicate five possible hydrogen bonds of lengths less than 2·80 Å and possibly two longer bonds of about 3·0 Å. The occurrence of two very short bonds about 2·4 Å indicates that the proton of the acid has been transferred to the water molecules, since a hydrogen bond between water molecules is normally about 2·76 Å. The equality of the S–O bonds in the sulphonate group also supports this conclusion. The hydrogen bond distances around O(*W*2) indicate that the extra proton is bonded to this water molecule to form an H_3O^+ ion. On this assumption the assignment of hydrogen atoms to the bonds is quite straightforward. O(*W*2) is bonded to two water molecules by very short bonds, O(*W*2)···O(*W*1), 2·419 Å and O(*W*2)···O(*W*3), 2·366 Å. The planar trigonal bonding coordination of the atom is completed by a bond to a sulphonate oxygen atom, O(1), 2·606 Å. The next nearest oxygen neighbour of O(*W*2) is 3·40 Å away.

H_2O(*W*1) has also a planar bonding coordination. The atom acts as hydrogen acceptor in one bond from O(*W*2), and as hydrogen donor in two bonds to sulphonate oxygen atoms, O(*W*1)···O(2), 2·706 Å and O(*W*1)···O(3), 2·694 Å. Other heavy atoms are all more than 3·50 Å away.

The third water molecule, H_2O(*W*3), has no near oxygen neighbours apart from O(*W*2). The nearest neighbours are two symmetry-related sulphonate oxygens, 2·99 and 3·05 Å away. The angles around O(*W*3) involving O(*W*2) and these two sulphonate oxygens are reasonable for hydrogen bonding and the two contacts O(*W*3)···O(2) may represent weak hydrogen bonds (see Fig. 4).

It is thus seen that the H_3O(*W*2)$^+$ ion and the water molecules H_2O(*W*1) and H_2O(*W*3) are held together by very strong hydrogen bonds to form an aggregate $[H_2O\cdots H_3O\cdots OH_2]^+$, which is best described as an $H_7O_3^+$ ion. This ion is hydrogen bonded to the sulphonate groups. No hydrogen bonds exist between individual $H_7O_3^+$ ions.

As can be seen from Fig. 3 and Table 2 the thermal ellipsoid of O(*W*2) is strongly elongated in the direction perpendicular to the bonds around O(*W*2). The thermal ellipsoids of O(*W*1), O(*W*3) and the sulphonate oxygen atoms also show a similar elongation. The orientations of the ellipsoids are shown in Fig. 3. However, it is not possible to distinguish from the present data whether these elongated ellipsoids indicate thermal motion, static disorder or systematic errors in the data. An O(*W*2) shift of 0·4 Å perpendicular to the bonds around O(*W*2) (which is consistent with the largest r.m.s. component of thermal motion) will change the $H_3O^+\cdots OH_2$ distances by only 0·03 Å. Similarly, as seen from Fig. 3 the elongation of the thermal ellipsoids of O(*W*1) and O(*W*3) is predominantly perpendicular to the O(*W*2)···OH_2 bonds. A moderate disorder of the atoms will thus still give rather short hydrogen bonds within the $H_7O_3^+$ aggregate.

The same behaviour for the thermal ellipsoid of the central oxygen atom in $H_7O_3^+$ was also found in $C_6H_3Br_2SO_3H.3H_2O$ (Lundgren, 1972) where the bonding coordination of the H_3O^+ ion and the water molecules is similar to that in the present compound. The two compounds are not isostructural, however. The compounds are being further investigated at this Institute using infrared spectroscopic techniques.

The 2,5-dichlorobenzenesulphonate ion

Bond distances and angles in the 2,5-dichlorobenzenesulphonate ion are given in Table 4 and Fig. 5, respectively. The C–H distances are calculated from the positions of the hydrogen atoms as obtained from the difference synthesis.

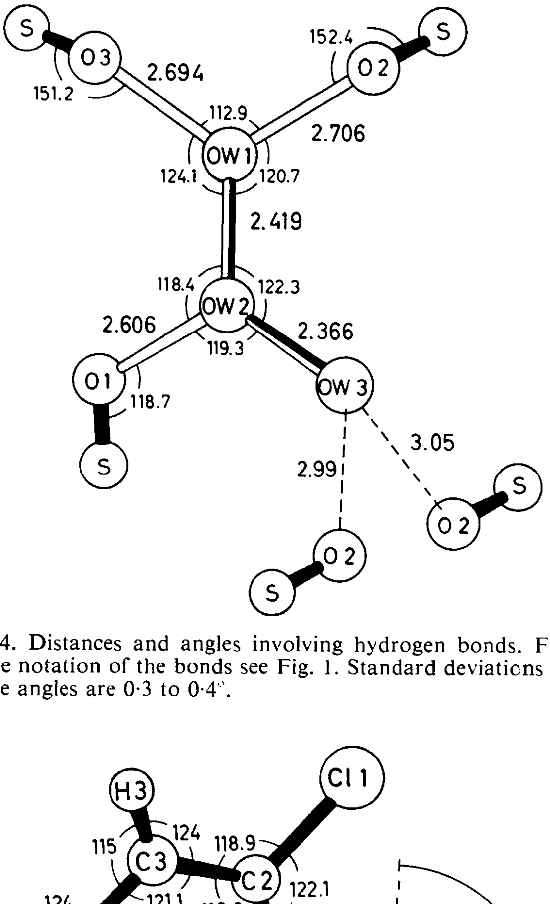

Fig. 4. Distances and angles involving hydrogen bonds. For the notation of the bonds see Fig. 1. Standard deviations of the angles are 0·3 to 0·4°.

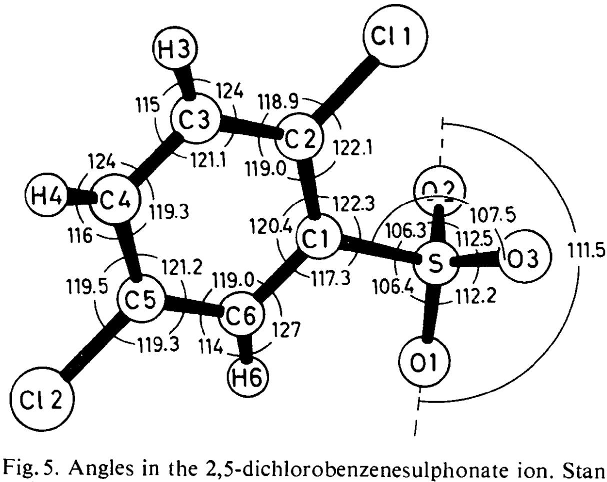

Fig. 5. Angles in the 2,5-dichlorobenzenesulphonate ion. Standard deviations of the angles not involving hydrogen atoms are 0·2 to 0·7°.

The benzene ring is a slightly distorted regular hexagon. The average C–C distance is 1·382 Å. The deviations of the atoms of the ion from the least-squares plane defined by the six carbon atoms are shown in Fig. 6. The carbon ring is not significantly different from planar. The least-squares plane was calculated using a method described by Blow (1960). The orientation of the sulphonate group with respect to the carbon ring is such that atom O(1) is nearly in the plane of the ring. The angle between the least-squares plane and the plane defined by C(1), S and O(1) is 0·7°. The average O–S–O and C–S–O angles in the sulphonate group are 112·1 and 106·2° respectively. These angles are similar to those found in 2,5-dibromobenzenesulphonic acid trihydrate, 112·5 and 106·2°. The S–O distances found in the present compound 1·448, 1·426 and 1·419 Å are somewhat shorter than the S–O distances in the bromo-compound, 1·463, 1·442 and 1·459 Å. (The distances are not corrected for thermal motion.)

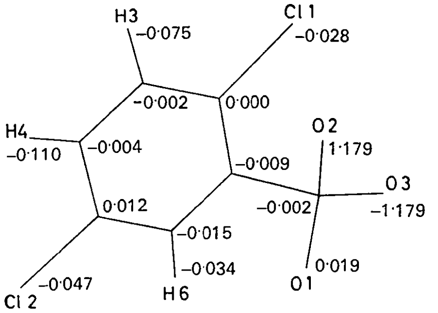

Fig. 6. Deviations of the atoms from the least-squares plane defined by the six carbon atoms of the 2,5-dichlorobenzene-sulphonate ion (Å).

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The Crystal Structures of Free Radical Salts and Complexes. I. (Morpholinium$^+$)$_2$(7,7,8,8-Tetracyanoquinodimethane)$_3^{2-}$

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Crystals of $(C_4H_{10}NO^+)_2(C_{12}H_4N_4)_3^{2-}$ are monoclinic, belonging to the space group $P2_1/c$, with lattice constants $a=7{\cdot}04$, $b=10{\cdot}67$, $c=26{\cdot}51$ Å, $\beta=96{\cdot}4°$, and having $Z=2$. The structure was solved from a three-dimensional Patterson synthesis and refined by block-diagonal least squares. It consists of columns of TCNQ molecules and anions packed plane-to-plane along the b axis. These columns are held together by the morpholinium ions through hydrogen bonding. The characteristic overlap and the short interplanar spacing of 3·25 Å indicate charge-transfer interaction between the TCNQ moieties.

Introduction

7,7,8,8-Tetracyanoquinodimethane (TCNQ) is a powerful electron acceptor and readily becomes the radical anion TCNQ$^-$ by accepting an additional electron. As such, it forms salts with cations of many types, inorganic, organic and radical cations. Many of these salts exhibit large specific conductances (Melby, Harder, Hertler, Mahler, Benson & Mochel, 1962) for organic crystals. In addition, a number of complex salts containing extra molecules of formally neutral TCNQ have even lower resistivities. Crystal structure determinations have already been reported for a number of these simple and complex radical-ion salts but no general picture of the relationship between structure and electrical properties has emerged. To assist in the elucidation of this relationship a number of further structure determinations are being carried