# The Crystal Structure of *p*-Benzenediazonium Sulphonate

CHR. RØMMING

Department of Chemistry, University of Oslo, Oslo 3, Norway

The crystal structure of *p*-benzenediazonium sulphonate, $N_2 - C_6H_4 - SO_3$, has been determined by X-ray methods using 1410 observed reflections collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 8.02_7$ Å; $b = 9.81_1$ Å; $c = 11.46_9$ Å; $\beta = 126.7_5°$. The refinements yielded a conventional R-factor of 0.052, estimated standard deviations are $0.002 - 0.004$ Å in bond lengths and $0.1 - 0.3°$ in bond angles. The charge distribution in the phenyldiazonium ion is discussed.

The crystal structure of *p*-benzenediazonium sulphonate has been reported by Sass and Lawson in 1970 [1,2] and has also been investigated in this laboratory. As the results of the measurements partly are in poor agreement,
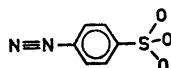
a full account of our investigation shall be given. The disagreement relates both to the unit cell parameters which deviate by more than 2 %, and to the atomic parameters. Sass and Lawson report that they had to use several crystal specimens during their data collection due to the instability of the compound towards X-radiation. Since no such difficulties were encountered during our experiments, the disagreement may rather be due to a different degree of purity in the samples. As Sass and Lawson obtained 521 reflections from film measurements and refined their model to an R-factor of 13 % whereas our diffractometer data comprised 1410 observed reflections with a final R of 5.2 %, we judge our results to be the more reliable.

EXPERIMENTAL

p-Benzenediazonium sulphonate was synthetized by the "inverted method"[3] from sulphanilic acid. Recrystallization from water yielded crystals well suited for the X-ray experiments. Oscillation and Weissenberg photographs showed the crystals to possess monoclinic symmetry. The systematic absences being $h0l$ with l odd and $0k0$ with k odd, the space group is $P2_1/c$.

Unit cell parameters were determined from diffractometer measurements for 19 general reflections on a Picker diffractometer using $CuK\alpha$ and $CuK\beta$ radiation ($\lambda = 1.5418$ Å and 1.3922 Å, respectively). The take-off angle was $0.5°$. The computer program used in the least-squares treatment of the measurements as well as programs applied during the rest of the structure analysis are described in Ref. 4.

A comparison of the cell parameters obtained in the present study and those given by Sass and Lawson is given below. Our values have been transformed to the space group $P2_1/n$ used by Sass and Lawson.

	a	b	c	β
Sass and Lawson [1,2]	8.10 Å	9.94 Å	9.46 Å	97.4°
Present study	8.02₇Å	9.81₁Å	9.26₃Å	97.2₂°

Three-dimensional intensity data were recorded on an automatic Picker diffractometer using Nb-filtered MoK-radiation. The take-off angle was $3°$, and the room temperature was kept constant at 17°C during the data collection. A crystal with approximate dimensions $0.5 \times 0.3 \times 0.2$ mm³ was mounted with a along the diffractometer ϕ-axis. The $\omega - 2\theta$ scanning mode with a 2θ scan speed of $2°$ min⁻¹ was applied through the scan range of $1°$ below $2\theta(\alpha_1)$ to $1°$ above $2\theta(\alpha_2)$. Background counts were taken for 35 sec at each of the scan range limits. Reflections for which the count rate exceeded 10^4 cps were remeasured with reduced primary beam intensity. The intensities of three standard reflections were measured for every 50 reflections of the data set; they decreased approximately uniformly by about 6 % during the data collection and the data were accordingly adjusted. The estimated standard deviations in the intensities were taken as the square root of the total counts with a 1 % addition for the uncertainty in the adjustment mentioned above.

Out of the 1981 unique reflections with $\sin \theta/\lambda < 0.70$, 1410 had intensities larger than 2.5 times the standard deviation. These were regarded as "observed" reflections whereas the remaining reflections were excluded from the refinement calculations.

The intensity data were corrected for Lorentz, polarization, and absorption effects.

Atomic form factors used were those of Hanson et al.[5] for bromine, nitrogen and carbon, and of Stewart et al.[6] for hydrogen.

CRYSTAL DATA

p-Diazoniumbenzene sulphonate, $N_2 \cdot C_6H_4 \cdot SO_3$, monoclinic.
$a = 8.027(0.004)$ Å; $b = 9.811(0.005)$ Å; $c = 11.469(0.005)$ Å; $\beta = 126.75(0.02)°$.
Figures in parentheses are estimated standard deviations.
$V = 723.75$ Å³; $M = 184.17$; $F(000) = 376$; $\mu = 0.41$ mm⁻¹; $Z = 4$.
$D_{obs} = 1.69$ g cm⁻³,[2] $D_{calc} = 1.690$ g cm⁻³.
Absent reflections: $h0l$ when l is odd, $0k0$ when k is odd, space group $P2_1/c$.

STRUCTURE DETERMINATION

The position of the sulphur atom was found by standard three-dimensional Patterson methods. A weighted Fourier synthesis [7] revealed the positions of all non-hydrogen atoms. The co-ordinates were refined by least-squares methods; anisotropic thermal parameters (using the expression $\exp -(B_{11}h^2 + B_{22}k^2 + B_{22}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$) were introduced and refined together with the positional parameters. Finally, positions of the hydrogen atoms were calculated and refined with isotropic thermal parameters. The last cycle of least-squares calculation gave shifts less than 10 % of the corresponding estimated standard deviations. The final conventional R-factor was 0.052 and the weighted R-factor 0.045.

A comparison of observed and calculated structure factors is given in Table 1; the final parameters for non-hydrogen atoms are listed in Table 2 and for hydrogen atoms in Table 3.

Table 1. Observed and calculated structure factors. The columns are h, k, l, $10 \times |F_o|$ $10 \times |F_c|$.

h	k	l	$10|F_o|$	$10|F_c|$
0	0	2	478	435
0	0	4	351	357
0	0	6	127	127
0	0	8	344	352
0	0	10	80	81
0	1	10	43	45
0	1	8	111	108
0	1	7	103	109
0	1	6	351	352
0	1	5	150	142
0	1	4	105	112
0	1	3	807	812
0	1	2	981	967
0	1	1	92	104
0	2	0	652	655
0	2	1	417	398
0	2	2	1.008	1.037
0	2	3	187	190
0	2	4	52	31
0	2	5	298	302
0	2	6	249	244
0	2	7	35	36
0	2	8	195	200
0	2	9	37	38
0	2	10	143	148
0	3	9	38	39
0	3	8	57	64
0	3	7	118	114
0	3	6	221	223
0	3	5	295	298
0	3	4	600	613
0	3	3	152	145
0	3	2	96	93
0	3	1	116	127
0	4	0	623	657
0	4	1	614	605
0	4	2	135	122
0	4	3	94	98
0	4	4	145	150
0	4	5	163	175
0	4	6	162	161
0	4	7	321	323
0	4	8	185	188
0	5	9	151	147
0	5	8	32	33
0	5	6	272	277
0	5	5	76	78
0	5	4	39	40
0	5	3	144	130
0	5	2	400	378
0	5	1	70	85
0	6	0	345	343
0	6	1	84	78
0	6	2	169	161
0	6	3	273	269
0	6	4	23	16
0	6	5	196	188
0	6	6	93	94
0	6	7	199	197
0	6	8	33	25
0	6	9	108	118
0	7	9	53	51
0	7	8	63	70
0	7	6	35	36
0	7	5	162	162
0	7	4	96	91
0	7	3	203	199
0	7	2	84	77
0	7	1	249	243
0	8	0	130	136
0	8	1	113	95
0	8	2	99	95
0	8	3	56	46
0	8	4	68	65
0	8	5	192	174
0	8	6	29	4
0	8	7	143	136
0	8	8	42	37
0	9	7	70	55
0	9	5	93	90
0	9	4	37	38
0	9	3	101	101
0	9	2	26	27
0	9	1	126	116
0	10	0	200	190
0	10	2	123	113
0	10	3	60	54
0	10	4	57	58
0	10	5	82	78
0	11	4	57	58
0	11	2	125	110
0	11	1	79	67
0	12	0	169	154
0	12	1	39	33
1	11	3	44	45
1	11	-4	70	63
1	11	-3	62	59
1	11	-2	112	99
1	11	-1	42	29
1	11	0	66	62
1	11	1	77	77
1	10	5	53	48
1	10	4	41	30
1	10	1	92	86
1	10	0	57	57
1	10	-1	129	121
1	10	-2	50	44
1	10	-4	43	45
1	10	-6	76	69
1	10	-7	34	31
1	9	-8	37	33
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1	9	-6	46	43
1	9	-5	76	70
1	9	-4	109	104
1	9	-3	118	110
1	9	-2	225	220
1	9	-1	58	61
1	9	0	152	161
1	9	1	107	100
1	9	2	62	68
1	9	3	213	199
1	9	4	52	50
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1	8	7	90	80
1	8	3	49	56
1	8	1	317	321
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1	8	-9	54	43
1	7	-7	169	161
1	7	-5	153	144
1	7	-4	57	59
1	7	-3	131	123
1	7	-1	129	129
1	7	0	102	116
1	7	1	321	308
1	7	2	35	36
1	7	3	195	190
1	7	4	102	103
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1	7	6	50	45
1	7	7	94	85
1	7	8	36	20
1	6	7	233	227
1	6	4	109	102
1	6	3	190	190
1	6	1	147	151
1	6	0	108	113
1	6	-2	323	332
1	6	-3	116	110
1	6	-3	24	18
1	6	-4	32	26
1	6	-5	68	66
1	6	-6	36	5
1	6	-8	30	36
1	6	-9	89	84
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1	5	-6	43	39
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1	5	-4	183	173
1	5	-3	314	301
1	5	-2	68	65
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1	5	4	93	92
1	5	5	368	361
1	5	6	57	60
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1	5	8	31	22
1	4	9	49	54
1	4	9	136	137
1	4	8	80	72
1	4	7	141	135
1	4	6	90	84
1	4	5	89	90
1	4	4	104	101
1	4	2	366	370
1	4	1	123	135
1	4	0	70	73
1	4	-1	109	98
1	4	-2	141	126
1	4	-3	171	152
1	4	-4	101	90
1	4	-5	67	73
1	4	-6	183	179
1	4	-7	135	133
1	4	-8	60	58
1	4	-9	88	87
1	4	-11	46	45
1	3	-10	100	107
1	3	-9	44	42
1	3	-8	170	177
1	3	-7	172	177
1	3	-6	84	82
1	3	-5	228	222
1	3	-4	101	99
1	3	-3	22	25
1	3	-2	73	81
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1	3	3	355	366
1	3	4	177	177
1	3	5	151	152
1	3	6	107	105
1	3	7	135	131
1	3	8	137	135
1	3	9	42	38
1	2	9	68	59
1	2	7	40	36
1	2	6	125	123
1	2	5	174	176
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1	2	2	33	27
1	2	1	374	368
1	2	0	473	493
1	2	-1	571	583
1	2	-2	293	269
1	2	-3	131	129
1	2	-4	78	68
1	2	-5	107	107
1	2	-6	94	84
1	2	-7	62	62
1	2	-8	159	166
1	2	-9	29	23
1	2	-10	45	52
1	2	-11	38	23
1	1	-10	88	92
1	1	-9	36	38
1	1	-8	171	181
1	1	-7	88	89
1	1	-6	179	186
1	1	-5	144	143
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1	1	-3	288	279
1	1	-2	747	683
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1	1	1	438	414
1	1	2	45	31
1	1	3	38	39
1	1	4	76	58
1	1	5	114	113
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1	1	10	40	39
1	0	6	114	115
1	0	4	32	16
1	0	2	207	220
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1	0	-4	181	167
1	0	-6	272	270
1	0	-10	50	45
1	0	-12	221	223
2	0	-10	136	137
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2	0	-6	146	141
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2	0	-2	701	605
2	0	0	875	859
2	0	2	54	59
2	0	6	54	49
2	0	8	118	118
2	1	6	197	201
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2	1	4	128	128
2	1	3	224	222
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2	1	1	107	104
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2	1	-4	323	323
2	1	-6	386	367
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2	1	-8	199	192
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2	2	-12	62	58
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2	2	-10	278	287
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2	2	-7	223	230
2	2	-6	312	312
2	2	-5	131	125
2	2	-4	143	115
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2	2	2	106	100
2	2	3	88	93
2	2	4	27	24
2	2	5	89	88
2	2	6	125	123
2	2	8	118	121
2	2	9	46	38
2	3	8	32	19
2	3	7	85	78
2	3	6	162	163
2	3	5	41	45
2	3	4	115	115
2	3	3	44	39
2	3	2	87	80
2	3	1	287	287
2	3	0	110	120
2	3	-1	171	185
2	3	-2	505	522
2	3	-3	195	181
2	3	-4	122	124
2	3	-6	250	244
2	3	-7	209	221
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2	4	-12	77	74
2	4	-11	62	64
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2	4	-9	38	40
2	4	-8	201	204
2	4	-7	185	192
2	4	-6	67	59
2	4	-5	310	315
2	4	-4	174	161
2	4	-3	128	120
2	4	-2	62	40
2	4	-1	17	5
2	4	0	307	326
2	4	1	262	259
2	4	2	56	55
2	4	3	174	169
2	4	6	69	61
2	4	8	79	69
2	5	7	64	58
2	5	6	58	61
2	5	5	58	50
2	5	4	92	92
2	5	3	91	88
2	5	2	130	142
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2	5	-1	214	225
2	5	-2	53	12
2	5	-5	240	241
2	5	-6	204	201
2	5	-7	144	144
2	5	-8	55	48
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2	5	-10	30	32
2	5	-11	59	53
2	6	-10	34	26
2	6	-9	72	74
2	6	-8	36	26
2	6	-7	191	185
2	6	-5	138	135
2	6	-4	75	63
2	6	-3	295	292
2	6	-2	214	219
2	6	-1	67	69
2	6	0	89	89
2	6	1	268	269
2	6	2	158	164
2	6	3	147	142
2	6	4	65	71
2	6	5	100	91
2	6	7	43	49
2	7	7	84	70
2	7	5	73	70
2	7	3	57	59
2	7	2	24	16
2	7	1	260	271
2	7	0	81	90
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2	7	-2	30	34
2	7	-3	73	78
2	7	-4	46	42
2	7	-5	61	53
2	7	-6	41	41
2	7	-7	44	34
2	7	-9	108	95
2	8	-7	162	146
2	8	-6	107	103
2	8	-5	121	114
2	8	-4	127	127
2	8	-3	128	117
2	8	-2	115	123
2	8	-1	74	81
2	8	0	29	25
2	8	1	170	159
2	8	2	72	74
2	8	3	86	79
2	8	5	98	81
2	8	6	57	54
2	9	5	77	63
2	9	4	77	75
2	9	1	98	102
2	9	-1	154	153
2	9	-3	34	39
2	9	-4	57	42
2	9	-7	72	64
2	10	-7	96	87
2	10	-6	42	37
2	10	-5	108	99
2	10	-4	104	94
2	10	-3	128	118
2	10	-2	109	118
2	10	-1	43	46
2	10	0	91	94
2	10	3	74	67
2	11	2	55	54
2	11	1	47	44
2	11	-1	54	50
2	11	-2	58	48
2	11	-4	62	60
3	11	-5	100	93
3	11	-1	41	32
3	11	0	82	84
3	10	2	130	123
3	10	-1	158	163
3	10	-2	111	110
3	10	-3	133	138
3	10	-4	40	42
3	10	-5	82	72
3	10	-6	126	105
3	9	-9	155	149
3	9	-7	166	149
3	9	-6	134	130
3	9	-5	209	200
3	9	-4	59	54
3	9	-3	154	156
3	9	-2	92	99
3	9	-1	205	209
3	9	0	106	109
3	9	1	107	98
3	9	3	108	98
3	8	5	71	72
3	8	4	104	92
3	8	3	52	48
3	8	2	38	29
3	8	1	97	107
3	8	0	61	65
3	8	-1	276	267
3	8	-3	405	426
3	8	-4	167	165
3	8	-5	124	116
3	8	-6	37	41
3	8	-7	29	13
3	8	-8	38	33
3	8	-9	77	73
3	7	-9	127	128
3	7	-8	101	106
3	7	-7	320	309
3	7	-6	153	149
3	7	-5	232	231
3	7	-4	43	46
3	7	-2	76	79
3	7	-1	118	128
3	7	0	190	207
3	7	1	316	317
3	7	3	167	164
3	7	5	91	82
3	6	4	53	49
3	6	4	46	44
3	6	2	52	55
3	6	2	40	41
3	6	1	211	219
3	6	0	113	119
3	6	-1	466	508
3	6	-2	41	45
3	6	-3	143	150
3	6	-4	114	119
3	6	-5	357	349

Table 1. Continued.

h	k	l	Fo	Fc
3	6	-6	81	85
3	6	-8	112	110
3	6	-9	253	256
3	6	-11	71	65
3	5	-10	70	72
3	5	-9	195	205
3	5	-8	137	140
3	5	-7	527	534
3	5	-6	34	27
3	5	-5	34	35
3	5	-4	96	92
3	5	-3	150	157
3	5	-2	264	288
3	5	-1	171	188
3	5	0	65	82
3	5	1	369	376
3	5	2	147	154
3	5	3	159	159
3	5	4	66	70
3	5	5	88	78
3	5	6	96	88
3	4	7	127	129
3	4	5	112	108
3	4	4	148	146
3	4	2	99	106
3	4	1	91	90
3	4	0	32	37
3	4	-1	333	358
3	4	-2	64	48
3	4	-3	291	288
3	4	-4	287	284
3	4	-5	48	49
3	4	-6	88	81
3	4	-8	67	61
3	4	-9	279	285
3	4	-10	159	162
3	4	-11	162	166
3	4	-12	43	43
3	3	-12	130	131
3	3	-9	214	219
3	3	-8	72	83
3	3	-7	120	124
3	3	-6	98	94
3	3	-5	317	304
3	3	-3	19	16
3	3	-2	90	97
3	3	-1	351	354
3	3	0	91	87
3	3	1	220	221
3	3	2	84	80
3	3	3	124	113
3	3	4	25	26
3	3	5	66	57
3	3	6	104	102
3	2	7	58	56
3	2	6	177	183
3	2	4	230	228
3	2	3	124	127
3	2	2	118	114
3	2	1	175	172
3	2	0	190	190
3	2	-1	515	508
3	2	-2	602	597
3	2	-3	516	498
3	2	-4	51	59
3	2	-5	235	225
3	2	-6	258	262
3	2	-7	73	66
3	2	-8	258	260
3	2	-9	25	22
3	2	-10	48	33
3	2	-11	55	48
3	2	-12	128	135
3	2	-13	77	78
3	1	-12	36	32
3	1	-11	75	75
3	1	-10	94	104
3	1	-9	80	89
3	1	-8	115	104
3	1	-7	153	157
3	1	-6	553	546
3	1	-5	61	62
3	1	-4	173	171
3	1	-2	418	419
3	1	-1	265	253
3	1	0	422	424
3	1	1	189	173
3	1	2	88	93
3	1	3	65	60
3	1	5	96	95
3	1	6	86	90
3	0	6	175	180
3	0	1	269	268
3	0	2	333	332
3	0	0	39	52
3	0	-2	373	355
3	0	-4	231	231
3	0	-8	345	343
3	0	-10	67	55
4	0	0	94	100
4	0	-8	83	80
4	0	-6	265	260
4	0	-4	293	289
4	0	-2	675	649
4	0	0	164	168
4	0	2	156	158

h	k	l	Fo	Fc
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4	1	6	62	59
4	1	5	47	41
4	1	3	220	215
4	1	3	26	27
4	1	2	270	270
4	1	1	207	207
4	1	0	540	534
4	1	-1	126	122
4	1	-3	173	165
4	1	-4	371	353
4	1	-5	180	180
4	1	-6	220	222
4	1	-7	150	145
4	1	-8	275	275
4	1	-9	25	38
4	2	-12	51	46
4	2	-10	136	140
4	2	-9	58	60
4	2	-8	80	88
4	2	-7	45	34
4	2	-6	144	154
4	2	-5	233	215
4	2	-4	69	67
4	2	-3	240	233
4	2	-2	293	285
4	2	0	39	19
4	2	1	78	75
4	2	2	70	77
4	2	3	98	98
4	2	4	200	203
4	2	5	61	57
4	2	6	139	135
4	3	6	35	39
4	3	4	121	117
4	3	3	47	35
4	3	2	342	341
4	3	1	83	86
4	3	0	145	149
4	3	-1	231	235
4	3	-2	61	62
4	3	-4	174	181
4	3	-5	159	151
4	3	-6	274	276
4	3	-7	92	86
4	3	-8	268	270
4	3	-9	111	116
4	3	-11	87	94
4	3	-13	52	45
4	4	-11	55	56
4	4	-10	115	124
4	4	-9	164	167
4	4	-8	70	68
4	4	-7	154	154
4	4	-6	144	133
4	4	-5	149	145
4	4	-4	71	72
4	4	-2	50	45
4	4	-1	75	62
4	4	-1	154	158
4	4	0	202	207
4	4	1	96	94
4	4	2	109	105
4	4	3	89	90
4	4	4	140	139
4	5	6	95	92
4	5	6	71	70
4	5	5	89	76
4	5	3	113	115
4	5	1	129	127
4	5	0	240	253
4	5	-1	154	153
4	5	-2	82	81
4	5	-3	176	183
4	5	-5	50	53
4	5	-6	24	16
4	5	-7	121	113
4	5	-8	78	74
4	5	-10	108	108
4	5	-11	93	94
4	6	-11	63	69
4	6	-9	163	165
4	6	-7	58	52
4	6	-6	99	92
4	6	-4	42	52
4	6	-3	78	90
4	6	-2	243	267
4	6	-1	210	227
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4	6	3	78	78
4	6	4	58	46
4	6	5	57	51
4	7	1	53	52
4	7	1	106	105
4	7	-1	89	97
4	7	-2	126	139
4	7	-3	209	227
4	7	-4	32	40
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4	7	-6	60	54
4	7	-7	111	110
4	7	-8	90	95
4	7	-11	65	64

h	k	l	Fo	Fc
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8	-6	148	149	
8	-5	90	97	
8	-4	36	34	
8	-3	49	53	
8	-2	60	67	
8	0	53	53	
8	1	140	133	
8	2	32	36	
9	2	59	51	
9	1	46	36	
9	0	73	68	
9	-1	134	132	
9	-2	35	27	
9	-3	45	45	
9	-4	88	89	
9	-5	109	112	
9	-6	58	44	
9	-7	113	104	
9	-8	97	87	
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10	-2	51	47	
10	-3	46	38	
10	-4	43	37	
10	-5	49	51	
10	-6	79	71	
9	9	119	108	
9	8	168	159	
9	-6	72	77	
9	-5	41	52	
9	-4	56	74	
9	-3	54	54	
9	-2	61	59	
9	-1	36	39	
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8	0	80	79	
8	-1	145	155	
8	-2	47	47	
8	-3	191	211	
8	-5	199	101	
8	-6	55	54	
8	-7	100	96	
8	-8	79	68	
8	-9	65	64	
7	-11	59	56	
7	-9	199	190	
7	-7	64	58	
7	-6	39	37	
7	-5	76	76	
7	-2	38	43	
7	0	61	60	
7	1	89	96	
6	1	42	45	
6	0	40	34	
6	-2	239	255	
6	-2	53	53	
6	-4	204	220	
6	-6	78	81	
6	-7	136	138	
6	-7	120	112	
6	-8	30	18	
6	-9	55	52	
6	-11	41	55	
6	-11	140	145	
5	-10	115	111	
5	-10	76	75	
5	-9	177	173	
5	-7	222	218	
5	-6	112	115	
5	-4	114	130	
5	-3	129	135	
5	-2	105	111	
5	0	84	89	
5	1	114	115	
5	1	78	78	
4	3	92	94	
4	2	41	41	
4	0	90	84	
4	-1	155	156	
4	-2	78	87	
4	-3	175	174	
4	-4	164	168	
4	-5	110	102	
4	-6	121	125	
4	-8	76	67	
4	-8	203	202	
3	-9	122	146	
3	-10	61	58	
3	-11	136	139	
3	-13	121	116	
3	-13	73	74	
3	-10	165	169	
3	-9	179	178	
3	-8	59	68	
3	-7	40	29	

h	k	l	Fo	Fc
5	3	-5	112	110
5	3	-2	160	158
5	3	0	82	82
5	3	1	28	25
5	3	2	38	40
5	3	3	76	71
5	2	5	60	54
5	2	4	90	86
5	2	3	82	79
5	2	1	29	17
5	2	0	288	287
5	2	-1	219	220
5	2	-2	61	57
5	2	-3	313	308
5	2	-4	194	185
5	2	-5	159	152
5	2	-6	256	257
5	2	-7	135	133
5	2	-8	370	374
5	2	-9	27	32
5	2	-10	106	98
5	2	-11	50	55
5	2	-13	56	48
5	1	-12	73	65
5	1	-10	168	177
5	1	-9	36	37
5	1	-8	26	23
5	1	-7	47	47
5	1	-6	179	175
5	1	-5	129	134
5	1	-4	94	97
5	1	-3	89	83
5	1	-2	209	207
5	1	-1	158	159
5	1	0	102	100
5	1	5	89	85
5	0	2	278	277
5	0	0	182	183
5	0	-2	142	143
5	0	-4	176	170
5	0	-6	193	183
5	0	-8	365	364
5	0	-10	129	110
5	0	-12	42	54
6	0	-14	153	167
6	0	-12	76	71
6	0	-10	95	97
6	0	-8	124	129
6	0	-6	436	430
6	0	-4	372	366
6	0	-2	180	169
6	0	0	121	118
6	0	0	34	28
6	1	2	159	163
6	1	1	38	37
6	1	0	270	266
6	1	-1	138	137
6	1	-2	265	263
6	1	-3	189	189
6	1	-4	132	135
6	1	-7	147	145
6	1	-7	152	151
6	1	-9	92	89
6	1	-10	246	245
6	1	-11	49	52
6	1	-12	113	107
6	2	-12	134	134
6	2	-10	163	165
6	2	-9	94	97
6	2	-8	171	170
6	2	-7	127	129
6	2	-6	230	230
6	2	-5	49	46
6	2	-4	139	134
6	2	-3	82	80
6	2	-2	234	234
6	2	-1	130	127
6	2	1	48	50
6	2	2	39	39
6	3	3	80	78
6	3	2	68	66
6	3	0	214	211
6	3	-1	93	94
6	3	-2	176	178
6	3	-3	249	243
6	3	-4	136	130
6	3	-5	129	129
6	3	-6	54	56
6	3	-7	105	104
6	3	-8	330	337
6	3	-9	55	44
6	3	-10	336	342
6	3	-11	53	66
6	3	-12	55	49
6	3	-13	48	48
6	4	-12	179	181
6	4	-12	127	126
6	4	-10	62	65
6	4	-10	68	75
6	4	-9	80	81
6	4	-8	160	161
6	4	-7	179	181
6	4	-6	92	92
6	4	-5	102	99

h	k	l	Fo	Fc
6	4	-4	158	166
6	4	-3	43	42
6	4	-2	142	140
6	4	1	97	96
6	5	2	65	70
6	5	0	97	103
6	5	-1	133	128
6	5	-2	63	68
6	5	-3	134	137
6	5	-4	67	75
6	5	-5	196	196
6	5	-6	61	69
6	5	-7	120	114
6	5	-8	100	106
6	5	-9	79	92
6	5	-10	81	80
6	5	-12	56	58
6	6	-10	33	12
6	6	-9	196	161
6	6	-7	90	95
6	6	-6	199	210
6	6	-5	50	47
6	6	-4	97	108
6	6	-3	39	35
6	6	-2	72	82
6	6	0	66	62
6	6	1	98	101
6	7	-1	117	123
6	7	-3	255	262
6	7	-5	110	120
6	7	-7	152	150
6	7	-8	63	65
6	7	-10	57	51
6	7	-11	50	49
6	8	-10	41	50
6	8	-9	68	58
6	8	-7	76	71
6	8	-7	50	45
6	8	-5	58	56
6	8	-1	101	100
6	9	-5	91	100
6	9	-5	75	86
7	8	-4	68	58
7	8	-5	167	181
7	8	-7	119	126
7	7	-9	152	146
7	7	-7	92	96
7	7	-4	63	68
7	7	-3	78	84
7	7	-2	54	46
7	6	-1	66	65
7	6	-3	134	136
7	6	-5	156	168
7	6	-6	35	52
7	6	-7	190	194
7	6	-11	55	71
7	5	-11	126	128
7	5	-9	188	192
7	5	-8	127	122
7	5	-7	107	99
7	5	-5	70	86
7	5	-4	82	82
7	5	-1	173	175
7	4	-1	87	84
7	4	-2	66	60
7	4	-3	221	225
7	4	-5	98	92
7	4	-7	117	113
7	4	-8	90	86
7	4	-9	109	108
7	4	-11	57	51
7	3	-12	156	178
7	3	-12	40	57
7	3	-10	38	35
7	3	-9	191	190
7	3	-8	40	53
7	3	-7	39	30
7	3	-6	156	155
7	3	-5	123	120
7	3	-3	70	82
7	3	-3	92	91
7	3	-1	88	82
7	3	0	57	54
7	2	0	143	133
7	2	1	93	56
7	2	-2	30	28
7	2	-3	138	138
7	2	-5	253	256
7	2	-6	32	29
7	2	-7	180	187
7	2	-8	155	155
7	2	-9	70	70
7	2	-10	59	48
7	2	-12	126	127
7	1	-13	36	40
7	1	-12	50	41
7	1	-11	37	41
7	1	-9	81	84
7	1	-8	196	197
7	1	-7	219	227
7	1	-6	37	44
7	1	-5	196	198

Table 1. Continued.

h	k	l	Fo	Fc
7	1	-4	78	74
7	1	-2	151	147
7	1	1	101	94
7	0	0	84	85
7	0	-2	316	309
7	0	-4	101	95
7	0	-6	220	216
7	0	-8	92	94
7	0	-10	277	277
8	0	-10	127	134
8	0	-12	73	65
8	0	-8	129	127
8	0	-6	193	191
8	0	-4	198	194
8	0	-2	206	198
8	1	-2	126	122
8	1	-3	36	25
8	1	-4	51	52
8	1	-5	89	88
8	1	-6	33	30
8	1	-8	163	171
8	1	-9	91	95
8	1	-10	174	177
8	1	-12	70	68
8	2	-12	131	131
8	2	-11	59	56
8	2	-10	47	47
8	2	-9	62	59
8	2	-8	31	28
8	2	-6	101	103
8	2	-5	38	44
8	2	-4	199	192
8	2	-3	37	33
8	2	-2	98	101
8	2	-1	56	63
8	3	-2	88	90
8	3	-3	89	88
8	3	-4	52	50
8	3	-6	95	101
8	3	-7	144	143
8	3	-8	135	129
8	3	-9	48	54
8	3	-10	194	205
8	3	-11	42	52
8	3	-12	92	88
8	4	-12	44	43
8	4	-11	100	94
8	4	-10	74	76
8	4	-9	193	188
8	4	-6	99	91
8	4	-7	109	109
8	4	-5	38	32
8	4	-4	88	93
8	4	-2	135	129
8	5	-4	46	37
8	5	-5	128	130
8	5	-7	90	99
8	5	-8	95	94
8	5	-9	50	48
8	5	-10	65	57
8	5	-11	55	59
8	6	-9	136	132
8	6	-7	89	88
8	6	-6	66	87
8	6	-4	35	37
8	7	-7	133	134
9	4	-7	132	129
9	4	-8	74	70
9	4	-9	90	92
9	4	-10	121	121
9	3	-11	93	84
9	3	-9	167	164
9	3	-8	83	78
9	3	-6	94	90
9	2	-4	83	84
9	2	-5	53	56
9	2	-6	56	50
9	2	-7	72	71

h	k	l	Fo	Fc
9	2	-8	53	43
9	2	-9	117	122
9	2	-10	131	136
9	1	-11	103	100
9	1	-8	131	128
9	1	-6	168	164
9	1	-4	176	168
9	0	-4	58	56
9	0	-8	89	86
9	0	-10	72	78
0	0	12	46	50
0	2	12	42	40
0	3	11	45	41
0	5	11	68	77
0	7	10	45	16
0	9	9	63	60
0	10	7	81	78
0	10	8	63	46
0	11	6	86	64
0	11	5	37	14
0	12	2	68	52
0	13	2	87	71
0	13	1	78	67
1	13	-4	62	50
1	13	-2	81	69
1	13	0	93	79
1	12	4	81	73
1	12	3	53	45
1	12	2	71	66
1	12	1	45	31
1	12	-1	87	71
1	12	-3	65	55
1	12	-4	81	75
1	12	-6	89	84
1	11	-8	78	68
1	11	5	134	113
1	11	6	99	78
1	10	7	123	106
1	10	6	79	73
1	10	-9	61	47
1	9	7	94	83
1	8	9	142	136
1	8	8	54	68
1	7	9	49	58
1	6	9	70	64
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1	4	11	42	36
1	3	-13	39	31
1	3	-12	41	42
1	3	10	64	57
1	3	11	63	73
1	1	-12	37	33
2	0	10	60	63
2	1	-14	107	116
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2	2	10	58	55
2	3	-13	38	25
2	5	9	59	60
2	5	-13	57	56
2	6	9	44	32
2	7	-11	39	22
2	9	7	68	59
2	9	-9	102	94
2	10	5	60	46
2	11	-6	79	73
2	11	-7	44	33
2	11	-8	59	52
2	12	-5	46	44
2	12	-3	65	55
2	12	-2	84	74
2	12	-1	47	41
2	12	0	53	52
2	13	-1	48	46
2	13	-4	47	51
3	13	-2	111	102
3	12	2	50	53
3	12	1	60	57
3	12	0	49	27

h	k	l	Fo	Fc
3	12	-1	86	82
3	12	-3	38	44
3	12	-4	98	88
3	12	-5	125	108
3	12	-6	46	40
3	11	-9	54	42
3	11	-8	47	35
3	11	-7	197	172
3	11	-6	52	47
3	11	1	152	144
3	11	3	70	61
3	10	5	61	54
3	10	3	48	46
3	10	-8	73	54
3	10	-9	99	95
3	9	5	95	87
3	8	7	80	70
3	8	-11	122	126
3	7	6	48	46
3	6	7	94	91
3	6	-12	40	26
3	6	-13	83	81
3	3	-14	81	94
3	3	8	99	106
3	1	-14	101	116
3	0	-14	70	71
4	0	8	67	74
4	1	8	85	89
4	1	7	47	51
4	2	-14	66	68
4	3	7	71	68
4	5	7	102	100
4	5	6	41	30
4	5	-13	81	85
4	6	6	64	62
4	7	5	36	34
4	7	-13	48	43
4	9	4	76	65
4	10	-9	93	87
4	10	-8	54	52
4	10	1	45	42
4	11	0	66	59
4	11	-1	63	63
4	11	-1	49	60
4	11	-4	99	105
4	11	-6	97	88
4	11	-8	64	53
4	12	-6	60	53
4	12	-5	50	36
4	12	-2	90	90
4	12	-1	40	50
5	12	-14	48	44
5	11	-5	70	71
5	11	-5	58	56
5	11	-2	57	61
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5	10	-8	60	55
5	10	-9	84	77
5	10	-10	97	55
5	9	-1	43	31
5	9	3	55	55
5	8	4	47	36
5	8	2	51	51
5	8	-11	103	100
5	7	-12	45	51
5	7	3	105	101
5	6	5	82	88
5	6	-13	122	122
5	6	-14	40	30
5	5	-14	63	59
5	4	5	83	79
5	3	-15	42	38
5	3	-14	62	63
5	3	5	44	23

h	k	l	Fo	Fc
5	3	6	72	67
5	2	-15	53	61
5	1	-14	68	72
6	0	4	52	52
6	1	4	73	77
6	2	-14	113	117
6	3	5	61	55
6	3	4	61	45
6	4	-14	60	70
6	4	3	78	70
6	4	4	43	46
6	5	3	65	67
6	6	-13	92	92
6	6	3	103	101
6	7	3	43	37
6	8	-12	40	47
6	8	-11	70	72
6	8	1	120	121
6	9	0	64	55
6	9	-1	105	108
6	9	-2	60	66
6	9	-10	69	58
6	10	-10	80	69
6	10	-9	96	87
6	10	-8	80	69
6	10	-7	55	52
6	10	-6	62	57
6	10	-5	47	50
6	10	-4	63	58
6	10	-1	46	60
6	11	-3	56	55
6	11	-6	42	48
6	11	-7	49	44
7	10	-5	76	80
7	10	-7	54	48
7	9	-9	111	100
7	9	-7	99	99
7	9	-6	45	36
7	9	-3	86	98
7	9	-2	57	69
7	9	-1	73	72
7	9	-2	48	58
7	8	-3	128	131
7	8	-10	54	45
7	8	-11	79	75
7	8	-12	46	15
7	7	-13	43	19
7	7	-1	150	150
7	7	1	92	102
7	6	1	138	136
7	6	0	40	31
7	6	-13	82	81
7	5	1	81	78
7	5	3	73	75
7	4	2	70	63
7	4	1	88	87
7	4	-13	48	49
7	4	-14	67	81
7	4	-15	55	48
7	3	-14	89	89
7	3	2	42	38
7	3	3	63	60
7	2	3	52	54
7	2	-14	88	66
7	2	-13	61	60
7	2	-15	41	35
7	0	2	41	35
7	0	-14	59	61
8	0	0	99	92
8	0	0	44	41
8	1	0	108	114
8	1	-14	61	67
8	2	-14	87	83
8	2	0	45	44
8	3	1	40	42
8	3	0	83	78
8	3	-13	51	40
8	3	-14	57	61
8	3	-15	60	74

h	k	l	Fo	Fc
8	4	-14	73	74
8	4	-1	55	49
8	4	0	39	41
8	5	0	71	72
8	5	-2	42	46
8	5	-13	67	74
8	6	-11	100	103
8	6	-3	86	81
8	7	-3	74	77
8	7	-5	79	89
8	7	-6	54	56
8	7	-9	48	68
8	7	-11	56	61
8	8	-11	63	62
8	8	-9	123	120
8	9	-7	73	74
9	7	-11	127	121
9	7	-9	86	82
9	6	-3	51	38
9	6	-4	45	37
9	6	-5	105	110
9	6	-7	97	98
9	6	-9	115	116
9	6	-11	65	62
9	5	-13	136	126
9	5	-12	40	23
9	5	-11	161	157
9	5	-9	112	103
9	5	-8	98	95
9	5	-7	66	76
9	5	-6	42	47
9	5	-4	40	34
9	5	-3	71	74
9	4	-6	67	68
9	4	-5	37	38
9	4	-14	53	48
9	3	-13	72	68
9	3	-12	77	86
9	3	-4	101	97
9	3	-2	41	28
9	3	-1	75	73
9	2	-2	74	76
9	2	-12	85	94
9	2	-13	38	39
9	1	-3	58	51
9	1	-2	88	79
9	0	-2	148	151
9	0	-14	116	123
10	0	-12	54	62
10	0	-10	49	51
10	0	-8	214	211
10	0	-6	171	160
10	1	-4	83	81
10	1	-5	53	59
10	1	-6	95	91
10	1	-7	48	39
10	1	-9	43	47
10	1	-10	148	147
10	1	-12	87	83
10	2	-12	88	94
10	2	-10	73	66
10	2	-8	155	147
10	2	-6	89	89
10	2	-4	97	88
10	3	-4	63	71
10	3	-10	123	118
10	3	-11	69	61
10	3	-12	75	83
10	4	-11	68	69
10	4	-9	59	53
10	4	-8	51	47
10	4	-6	104	104
10	5	-8	39	44
10	5	-9	89	92
10	5	-11	64	39
11	1	-10	81	78

Magnitudes and directions of the principal axes of the ellipsoids of vibration are given in Table 4. Rigid-body motion analysis were made considering the complete molecule (I), the benzenediazonium part (II), and the $C-SO_3$ group (III) as the rigid units. The r.m.s. discrepancy between the atomic vibration tensor components arrived at in the structure analysis and those calculated from the rigid-body parameters obtained are 0.0031 Å², 0.0023 Å², and 0.0015 Å², respectively. The sets of eigenvalues for **T** are nearly identical for the three models. The largest amplitude of librational motion was found to be about an axis parallel to the axis of the lowest inertia, the $N-N-Cl-$

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^4$).

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	2826	2142	501	140	56	85	−1	153	3
	1	1	1	2	1	1	3	2	2
O1	2639	793	−55	226	75	155	−67	259	−72
	3	2	2	7	3	4	7	9	5
O2	3118	2168	1875	332	138	113	−110	318	−32
	4	3	2	8	3	3	9	9	6
O3	1201	3068	−555	167	106	153	58	169	98
	3	2	2	6	3	4	7	8	6
N1	10560	4478	1829	160	79	90	43	161	5
	4	3	3	7	3	4	8	9	6
N2	12008	4910	2105	191	114	143	−6	242	−14
	4	3	3	8	4	5	10	11	7
C1	8696	3913	1479	123	71	85	12	142	15
	4	3	3	8	4	4	9	12	7
C2	7813	4567	2063	181	76	106	−27	191	−44
	5	4	4	9	4	5	11	12	8
C3	6021	4003	1747	186	78	115	2	225	−36
	5	3	4	9	4	5	10	12	8
C4	5178	2840	885	132	62	66	34	121	23
	4	3	3	7	3	4	10	9	7
C5	6105	2239	323	161	72	83	−14	150	−34
	5	4	3	8	4	4	10	10	7
C6	7913	2767	615	160	89	90	21	172	−14
	5	3	3	8	4	4	11	10	8

Table 3. Fractional atomic coordinates ($\times 10^3$) and thermal parameters with estimated standard deviations for hydrogen atoms.

Atom	x	y	z	B
H2	846	532	270	2.1
	4	3	3	.7
H3	546	443	214	3.7
	5	3	3	.8
H5	550	146	−22	2.2
	4	3	3	.7
H6	867	240	25	2.3
	4	3	3	.6

C4−S direction in the molecule, the r.m.s. angles being 8.3° (I), 7.2° (II), and 9.2° (III). The other two amplitudes were small in all cases. The librational motion of the molecule may thus be described as an oscillation of the benzene ring with an r.m.s. amplitude of 7.2° about the C1 − C4 diagonal and an oscillation with a somewhat larger amplitude (9.2°) of the SO_3 group about the C4 − S single bond.

Bond lengths, their estimated standard deviations, the bond lengths corrected for thermal effects, valence angles and *inter*-molecular distances may be found in Table 5. The thermal corrections applied are those according

Table 4. R.m.s. amplitudes of vibration $(\overline{u^2})^{\frac{1}{2}}$ (Å) and *B*-values (Å²) along the principal axes of vibration given by the components of a unit **e** in fractional coordinates ($\times 10^4$).

Atom	$(u^2)^{\frac{1}{2}}$	B	e_x	e_y	e_z
S	.191	2.89	1054	59	1080
	.166	2.18	231	−1006	45
	.152	1.82	1119	152	−122
O1	.272	5.82	830	−416	993
	.197	3.06	−1185	150	54
	.171	2.31	570	918	441
O2	.294	6.81	1143	−689	519
	.230	4.19	998	730	657
	.150	1.79	340	175	−695
O3	.298	7.01	273	528	844
	.205	3.32	779	698	−136
	.174	2.39	1318	−522	673
N1	.208	3.41	879	840	342
	.195	3.00	734	−299	1032
	.156	1.93	−1052	494	43
N2	.250	4.94	816	−420	991
	.233	4.29	427	928	449
	.170	2.29	1253	−43	9
C1	.198	3.09	688	632	853
	.178	2.52	563	−799	675
	.144	1.63	1276	12	36
C2	.228	4.12	789	−562	908
	.183	2.64	1269	564	388
	.167	2.19	−428	637	458
C3	.232	4.25	914	−448	975
	.197	3.05	964	799	379
	.142	1.60	−808	446	301
C4	.189	2.81	908	761	658
	.158	1.96	392	210	−660
	.153	1.85	1200	−645	562
C5	.208	3.40	562	−722	764
	.180	2.56	1443	342	463
	.160	2.02	−139	633	621
C6	.215	3.66	50	944	−307
	.198	3.09	1268	197	1007
	.150	1.77	−899	330	277

to model II for the benzenediazonium part of the molecule, model III for the SO$_3$ group and model I for the C−S bond. Standard deviations were calculated from the correlation matrix ignoring the uncertainty in cell parameters.

DISCUSSION

The geometry of the *p*-benzenediazonium sulphonate as found in the present analysis is shown in Fig. 1 in which the numbering of the atoms also is indicated. Except for the oxygen atoms the molecule is nearly planar with two-fold symmetry about the main molecular axis. The deviations of the carbon atoms from a least-squares plane defined by the benzene ring are all less than 0.004 Å whereas the deviation from this plane of S, N1, and N2 are 0.003 Å, 0.028 Å, and 0.056 Å, respectively.
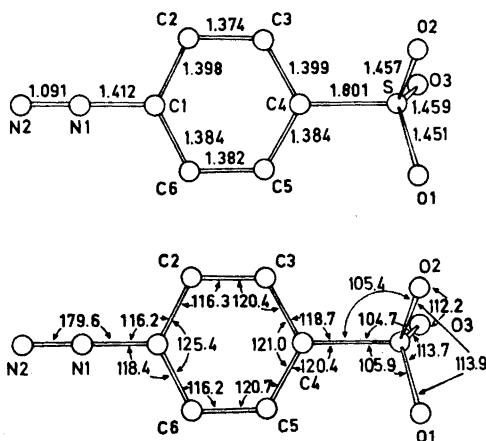
Fig. 1. Bond lengths (corrected) (Å) and angles (°).

The bond lengths and angles of the sulphonate group are quite normal. The arrangement about the sulfur atom is distorted tetrahedral with a mean C−S−O angle of 105.3° and a mean O−S−O angle of 113.3°, in good agreement with the corresponding values of 105° and 113° in 2-diazonium-4-phenol-sulphonate monohydrate [8] and 106.3° and 112.3° in the o-carboxybenzene-sulphonate ion.[9] The orientation of the (nearly trigonal) −SO$_3$ group about the C4−S bond is probably mainly determined by the crystal forces. The O1−H5 distance is 2.51 Å, which is about the expected van der Waals separation. The angles between the plane of the benzene ring and the planes defined by C4, S, and the oxygen atoms are 15.7° (O1), 43.8° (O2), and 74.6° (O3), respectively.

The benzenediazonium part of the molecule has the characteristical features of the benzenediazonium ions examined earlier in this laboratory. The C−N−N group is linear with N−N bond length 1.091 Å and a C−N bond of 1.413 Å as compared with 1.097 Å and 1.39 Å in benzenediazonium chloride,[10] 1.098 Å and 1.425 Å in benzenediazonium chloride-acetic acid [11] and 1.09 Å and 1.42 Å in p-benzenetetrazonium tetrachlorozincate.[12] The internal angle of 125.4° at C1 seems also to be normal for this kind of compound, as are the angles of 116.2° at C2 and 116.3° at C6.

The quinoid character of the benzene ring suggested by Sass and Lawson [2] might just possibly be verified by the present structure determination, the average bond lengths of C1−C2, C3−C4, C4−C5, and C6−C1 being 1.391 Å and that of C2−C3 and C5−C6 being 1.378 Å. The large difference between their corresponding values, 1.44 Å and 1.38 Å, respectively, is probably due to poor quality in the experimental data rather than being a real effect from a quinoid contribution to the structure, and is indeed not significant according to the estimated standard deviations of their coordinates.

The crystal structure is mainly governed by electrostatic forces between the positively charged diazonium groups and the negative sulphonate groups

of neighbouring molecules. Each diazonium group is surrounded by three oxygen atoms from different molecules in a distorted trigonal arrangement in a plane nearly normal to the N−N bond between the nitrogen atoms. The separations of the nitrogen and oxygen atoms are listed in Table 5. The shortest contact is 2.73 Å between an N1 and an O3 atom. This is 0.17 Å less than the expected van der Waals distance.

Table 5. Bond lengths, corrected bond lengths, bond angles and *inter*-molecular distances. Estimated standard deviations (in parentheses) apply to the least significant digits.

Bond distances (Å)		Corrected	Bond angles (°)	
N2−N1	1.091(3)	1.091	N2−N1−C1	179.6(3)
N1−C1	1.410(4)	1.412	C6−C1−C2	125.4(3)
C1−C2	1.390(4)	1.398	N1−C1−C6	118.4(3)
C2−C3	1.371(4)	1.374	N1−C1−C2	116.2(3)
C3−C4	1.392(4)	1.399	C1−C2−C3	116.3(3)
C4−C5	1.376(4)	1.384	C2−C3−C4	120.4(3)
C5−C6	1.380(4)	1.382	C3−C4−C5	121.0(3)
C6−C1	1.377(4)	1.384	C4−C5−C6	120.7(3)
C4−S	1.798(3)	1.801	C5−C6−C1	116.2(3)
O1−S	1.438(2)	1.451	C3−C4−S	118.7(2)
O2−S	1.449(2)	1.457	C5−C4−S	120.4(2)
O3−S	1.450(2)	1.459	C4−S−O1	105.9(1)
C2−H2	0.95(3)		C4−S−O2	105.4(1)
C3−H3	0.91(3)		C4−S−O3	104.7(1)
C5−H5	0.92(3)		O1−S−O2	113.9(1)
C6−H6	0.99(3)		O2−S−O3	112.2(1)
			O1−S−O3	113.7(1)

Short *inter*-molecular distances (Å)

N1−O1 (1+x, $\frac{1}{2}-y$, $\frac{1}{2}+z$)	2.914
N2−O1 » » »	3.060
N1−O2 (1+x, y, z)	3.037
N2−O2 » » »	2.895
N1−O3 (1−x, 1−y, −z)	2.731
N2−O3 » » »	2.873
H5−O1 (1−x, −y, −z)	2.581
H2−O2 (1−x, +y, $\frac{1}{2}+z$)	2.421
N2−C5 (2−x, $\frac{1}{2}+y$, $\frac{1}{2}-z$)	3.297

The charge distribution in the benzenediazonium ion has been the subject of some discussion by several authors. From geometrical consideration on the results of the structure determination of benzenediazonium chloride the present author [10] concluded that the positive charge is shared between the nitrogen atoms, and that an electron transfer from the phenyl ring to the nitrogen atoms is likely. Porai-Koshits [13] finds a contradiction between the presence of a pure triple nitrogen−nitrogen bond implying a positive charge on the *inner* nitrogen atom and the implication he finds from X-ray structure data that the larger part of the positive charge is situated at the *outer* nitrogen atom.

The complete neglect of differential overlap method (CNDO) was employed in order to calculate the net charge on the atoms. A description of the standard

version CNDO/2 is given in Ref. 14, which also gives the parameters needed in the calculations; the molecular geometry used was that found in the present structure determination. The calculated atomic net charges were as follows:
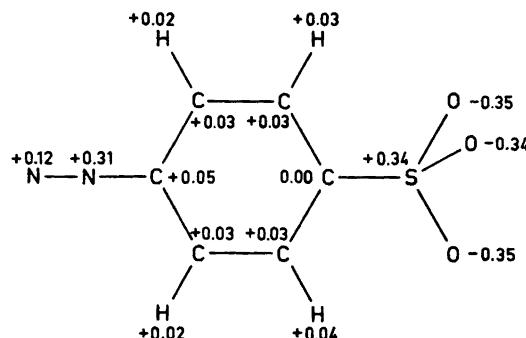
It must be emphasized, however, that the calculations apply to a free molecule, and that the charge distribution may be different in the strong electrical field present in the crystal.

When calculations are performed for the free benzenediazonium ion with the geometry as found in benzenediazonium chloride,[10] rather similar results to those given above for the phenyldiazonium part are obtained. The charge on the outher nitrogen atom was found to be $+0.18$ and on the inner 0.31; the rest of the positive charge, $+0.51$, was evenly distributed among the phenyl atoms. A calculation was also made on the same ion with a crystal field simulated by placing four negative ions (fluorine) in positions relative to the diazonium group corresponding to those of the benzenediazonium chloride structure. This resulted in a relative displacement of electrons from the outer nitrogen atom towards the opposite part of the benzene ring, the net charge on the nitrogen atoms being $+0.25$ (outer) and $+0.33$ (inner). A calculated net charge of $+0.11$ on the *ortho* hydrogen atoms may explain the $C-H\cdots Cl^-$ hydrogen bond actually observed in the benzenediazonium chloride structure.

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