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The Crystal Structure of *p*-Benzenebisdiazonium Tetrachlorozincate

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The crystal structure of *p*-benzenebisdiazonium tetrachlorozincate, $N_2C_6H_4N_2 \cdot ZnCl_4$, has been determined by three-dimensional X-ray methods. The crystals are tetragonal, space group $P\bar{4}2_1m$, and the unit cell, containing two formula units, has the dimensions:

$$a = 10.511 \text{ Å}; \qquad c = 5.249 \text{ Å}$$

The intensity data were collected using integrating Weissenberg techniques. 286 independent reflections were used for the structure determination. The structure model was refined by least-squares methods to a conventional R value of 6.5 %.

The tetrachlorozincate ions are situated on four-fold inversion axes. They are approximately tetrahedral with Zn—Cl distances of 2.283 Å (e.s.d. 0.002 Å) and with Cl—Zn—Cl angles of 117.0° and 105.8° (e.s.d. 0.2°).

The *p*-benzenebisdiazonium ion has *mm* symmetry and is, within the accuracy of the measurement planar, with a linear N—N—C···C—N—N arrangement. The N≡N and N—C bonds are 1.09 Å and 1.42 Å, respectively, with estimated standard deviations of 0.01 Å. A deviation from hexagonal symmetry of the carbon ring is discussed.

A common feature of the structure of aromatic diazonium salts so far investigated[1-3] is a deformation of the benzene ring to which the N_2^+ group is attached. The C(2)—C(1)—C(6) angle is significantly larger than 120°, an effect which has been attributed to the strong electrophilic character of the diazonium group.[1]

The deformation of a benzene ring with *two* diazonium substituents would be expected to be still more pronounced. In order to study this effect a *para*-benzenebisdiazonium salt was chosen as the object for the present investigation.

Since the diazotisation of the second amino group in *p*-phenylenediamine is not possible by conventional methods, it is necessary to use a concentrated mineral acid as the solvent in the reaction and to tetrazotize with nitrosylsulphuric acid. Because the crystalline tetrazonium salts of simple acids, *e.g.* the chloride, are extremely explosive, we stabilized the compound by forming a double salt with an inorganic halide. The anion selected was the tetrachlorozincate, which forms relatively stable tetrazonium salts, although this leads to a somewhat lower accuracy in the parameter determination in the tetrazonium ion than a lighter anion.

EXPERIMENTAL

p-Phenylenediamine was tetrazotized with nitrosylsulphuric acid in concentrated phosphoric acid according to the Schoutissen method.[4] To the reaction mixture was added a cold solution of zinc chloride in phosphoric acid (85 %). After stirring for some time the tetrachlorozincate precipitated and was isolated by centrifugation. The salt was washed with phosphoric acid and ether and purified by dissolving it in cold formic acid, and subsequent reprecipitation with cold anhydrous ether. (Found: C 21.22; H 1.29; N 16.38; Zn 20.86; Cl 40.38. Calc. for $C_6H_4N_4ZnCl_4$: C 21.24; H 1.19; N 16.51; Zn 19.29; Cl 41.49).

The compound is explosive, decomposes quickly in a humid atmosphere or by exposure to light. It may, however, be kept for months when stored in darkness and kept dry and cold.

Crystals suitable for the X-ray experiments were obtained by slow diffusion of ether into a formic acid solution of the salt; they were pale-yellow, thin square plates. The specimens chosen had dimensions of $0.2 \times 0.2 \times 0.02$ mm³.

The unit cell dimensions were determined by least-squares methods from the positions of eight strong lines on a Guinier photograph taken at room temperatures with $CuK\alpha_1$ radiation ($\lambda = 1.54050$ Å).

The intensity data were obtained using multifilm integrating equi-inclination Weissenberg technique with Ni-filtered $CuK\alpha$ radiation at temperatures in the interval -10 to -20°C. The layers $0kl-4kl$ and $hk0-hk3$ were recorded; owing to the poor stability of the compound a new crystal had to be mounted for each layer line exposure. The intensities were measured photometrically except for the weakest reflections which were estimated visually with use of a calibrated scale. Out of the 321 independent reflections obtainable with $CuK\alpha$ radiation 286 reflections might occur on the recorded layers. Of these 221 were actually observed to be above the background level.

The intensities were corrected for absorption effects and, prior to the last stages of the refinement procedure, for secondary extinction by the method given by Zachariassen [5] and by Åsbrink and Werner.[6]

The full-matrix least-squares program used in the parameter refinement procedure was written by Gantzel, Sparks and Trueblood (IUCr. World List No. 384), modified to include a weight analysis and adapted for a UNIVAC 1107 computer. The program minimizes the function $\sum w(F_{\text{obs}}-G\cdot F_{\text{calc}})^2$; the weight ($w^{\frac{1}{2}}$) applied to the structure factors was constant for $|F_{\text{obs}}| \leqslant 9$ and proportional to $|F_{\text{obs}}|^{-\frac{1}{2}}$ for larger values of $|F_{\text{obs}}|$. Non-observed reflections were included with a structure factor corresponding to the most probable value [7] and assigned a weight of one-third of the weight given to the observed reflections.

The atomic form factors used in the calculations were those given by Hanson *et al.*[8] for neutral atoms.

CRYSTAL DATA

p-Benzenebisdiazonium tetrachlorozincate, $C_6H_4N_4Cl_4Zn$, decomposes if heated.

Tetragonal, unit cell dimensions:

$$a = 10.511(0.004) \text{ Å}; \qquad c = 5.249(0.009) \text{ Å}$$

Figures in parenthesis are estimated standard deviations.

$V = 579.9$ Å³, $M = 339.31$, $F(000) = 332$, $Z = 2$.

Calculated density at room temperature: 1.934 g.cm^{-3}

Absent reflections: $h00$ when $h = 2n + 1$.

Space group: $P42_12$ or $P\bar{4}2_1m$

STRUCTURE DETERMINATION

The space groups compatible with the systematically absent reflections are $P42_12$ and $P\bar{4}2_1m$, and the number of formula units per unit cell is *two*. The former space group requires either a 222 symmetry of the tetrachlorozincate ion, in which case *two* ions have to be situated along the short *c*-axis, or this ion has to be planar with a four-fold axis of symmetry. Since a tetrahedral arrangement in this ion is expected, the second space group, $P\bar{4}2_1m$ was thought to be more probably correct, and the structure determination and refinement was based on this assumption. In this space group a $\bar{4}$ symmetry is demanded of the tetrachlorozincate ion with the zinc atom in a four-fold centre of inversion; the tetrazonium ion must possess *mm* symmetry.

A well resolved *c* projection was to be expected; the initial structure determination was therefore based on the *hk*0 reflections. Approximate parameters were found from a sharpened Patterson map and refined by successive Fourier syntheses to a conventional *R* factor of 0.09.

Assuming a planar tetrazonium ion, the only positional parameters left to be determined were the *z* parameter of this ion and of one chlorine atom. An estimate of these parameters was possible from an analysis of the *h*0*l*-data. Using *x*-parameters from the *c* projection, refinements of the two *z*-parameters gave an *R* value of 0.13. Three-dimensional refinement was then initiated by least-squares methods.

During the early refinement cycles the zinc and chlorine atoms were assigned anisotropic, and the carbon and nitrogen atoms isotropic temperature factors. After a couple of cycles the individual layer line data were rescaled, and the refinement was continued with anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atom was also included in the calculation, the parameters were not varied, but the position was fixed in the plane of the benzene ring at a distance of 1.03 Å from the carbon atom in a direction bisecting the corresponding benzene angle. A *B* value of 4.0 Å^2 was assigned to the isotropic temperature factor.

The refinement brought the *R* index down to 0.07. After the intensity data were corrected for secondary extinction and the refinement procedure repeated with non-observed reflections included, the resulting *R* value was 0.065. 286 reflections were used in the determination of 12 positional and 26 thermal parameters.

Table 1. Final parameters and their estimated standard deviations (in parenthesis). The values have been multiplied by 10^4. The temperature factor is of the form exp $-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. The figures for hydrogen are assumed values.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{33}
Zn	0	0	0	47(1)	(B_{11})	320(10)	0	0	0
Cl	0567(2)	1764(2)	7270(5)	48(2)	39(2)	266(8)	0(3)	19(9)	30(8)
N(1)	2573(9)	($\frac{1}{2}$-x)	2290(33)	58(8)	(B_{11})	390(63)	10(20)	−80(39)	($-B_{13}$)
N(2)	1834(8)	($\frac{1}{2}$-x)	2350(27)	39(6)	(B_{11})	270(44)	−20(17)	−40(33)	($-B_{13}$)
C(1)	0878(9)	($\frac{1}{2}$-x)	2290(31)	40(7)	(B_{11})	260(49)	10(19)	30(34)	($-B_{13}$)
C(2)	1307(8)	5353(9)	2290(33)	37(8)	37(8)	260(36)	10(12)	10(31)	30(36)
H	2262	5573	2290						

Table 2. Observed and calculated structure factors. The columns are h, k, l, $10|F_{\mathrm{obs}}|$ and $10|F_{\mathrm{calc}}|$. Asterisks indicate non-observed reflections.

0	0	1	423	552	
0	0	2	1145	1174	
0	0	3	250	254	
0	0	4	853	846	
0	0	5	241	224	
0	0	6	132	130	
1	0	1	336	316	
1	0	2	161	189	
1	0	3	113	94	
1	0	4	165	156	
1	0	5	35	22	
1	0	6	95	98	
1	1	0	556	603	
1	1	1	539	657	
1	1	2	368	388	
1	1	3	106	126	
1	1	4	319	298	
1	1	5	260	277	
1	1	6	99	92	
2	0	0	452	492	
2	0	1	473	524	
2	0	2	430	453	
2	0	3	242	282	
2	0	4	239	210	
2	0	5	165	144	
2	0	6	81	77	
2	1	0	285	284	
2	1	1	598	566	
2	1	2	220	208	
2	1	3	315	284	
2	1	4	135	120	
2	1	5	137	117	
2	1	6	66	65	
2	2	0	259	305	
2	2	1	660	719	
2	2	2	536	564	
2	2	3	531	556	
2	2	4	171	162	
2	2	5	152	138	
2	2	6	139	136	
3	0	1	906	877	
3	0	2	127	126	
3	0	3	494	461	
3	0	4	139	135	
3	0	5	203	193	
3	0	6	83	93	
3	1	0	249	267	
3	1	1	682	716	
3	1	2	549	558	
3	1	3	470	494	
3	1	4	134	121	
3	1	5	122	118	
3	1	6	107	116	
3	2	0	417	424	
3	2	1	266	245	
3	2	2	318	298	
3	2	3	176	152	
3	2	4	165	141	
3	2	5	98	89	
3	2	6	58	52	
3	3	0	65	40	
3	3	1	457	495	
3	3	2	644	658	
3	3	3	386	417	
3	3	4	33	34	
3	3	5	64	67	
3	3	6	104	139	
4	0	0	431	434	
4	0	1	380	426	
4	0	2	388	387	
4	0	3	257	281	
4	0	4	180	166	
4	0	5	121	121	
4	0	6	97	86	
4	1	0	399	398	
4	1	1	101	98	
4	1	2	313	302	
4	1	3	171	171	
4	1	4	181	164	
4	1	5	126	136	
4	1	6	75	70	
4	2	0	30	13	
4	2	1	380	442	
4	2	2	629	638	
4	2	3	209	223	
4	2	4	71	61	
4	2	5	138	141	
4	2	6	136	121	
4	3	0	359	349	
4	3	1	122	102	
4	3	2	282	259	
4	3	3	87	76	
4	3	4	149	134	
4	3	5	46	53	
4	3	6	48	57	
4	4	0	380	381	
4	4	1	532	561	
4	4	2	356	364	
4	4	3	374	362	
4	4	4	265	267	
4	4	5	158	164	
4	4	6	120	167	
5	0	1	345	335	
5	0	2	96	105	
5	0	3	227	197	
5	0	4	131	118	
5	0	5	95	82	
5	0	6	80	80	
5	1	0	721	706	
5	1	1	423	457	
5	1	2	123	118	
5	1	3	238	240	
5	1	4	329	288	
5	1	5	150	161	
5	1	6	35	49	
5	2	0	540	557	
5	2	1	64	48	
5	2	2	426	423	
5	2	3	106	92	
5	2	4	267	225	
5	2	5	93	81	
5	2	6	103	96	
5	3	0	691	745	
5	3	1	386	412	
5	3	2	109	84	
5	3	3	251	243	
5	3	4	307	311	
5	3	5	126	146	
5	4	0	244	250	
5	4	1	59	36	
5	4	2	209	189	
5	4	3	70	17	*
5	4	4	100	95	
5	4	5	19	5	*
5	5	0	112	117	
5	5	1	662	644	
5	5	2	399	406	
5	5	3	458	428	
6	0	0	434	435	
6	0	1	351	369	
6	0	2	237	223	
6	0	3	196	177	
6	0	4	239	207	
6	0	5	139	140	
6	1	0	211	181	
6	1	1	408	362	
6	1	2	191	168	
6	1	3	273	235	
6	1	4	130	130	
6	1	5	124	118	
6	2	0	681	705	
6	2	1	437	454	
6	2	2	103	85	
6	2	3	225	212	
6	2	4	343	308	
6	2	5	205	197	
6	3	0	165	157	
6	3	1	81	67	
6	3	2	142	122	
6	3	3	81	61	
6	3	4	73	64	
6	3	5	47	45	
6	4	0	329	331	
6	4	1	318	333	
6	4	2	227	222	
6	4	3	204	182	
6	4	4	181	169	
6	4	5	114	125	
6	5	0	195	182	
6	5	1	110	93	
6	5	2	187	154	
6	5	3	113	116	
6	6	0	188	192	
6	6	1	340	328	
6	6	2	267	260	
6	6	3	323	335	
7	0	1	268	254	
7	0	2	52	50	
7	0	3	194	167	
7	0	4	86	60	
7	0	5	84	79	
7	1	0	268	233	
7	1	1	424	422	
7	1	2	311	315	
7	1	3	309	294	
7	1	4	147	123	
7	1	5	104	112	
7	2	0	22	30	
7	2	1	100	88	
7	2	2	57	55	
7	2	3	68	66	
7	2	4	66	58	
7	2	5	35	40	
7	3	0	443	441	
7	3	1	370	379	
7	3	2	144	121	
7	3	3	209	183	
7	3	4	210	209	
7	3	5	129	173	
7	4	0	344	314	
7	4	1	81	66	
7	4	2	283	257	
7	4	3	131	128	
7	4	4	154	147	
7	4	5	97	115	
7	5	0	56	56	
7	5	1	274	274	
7	5	2	356	358	
7	5	3	230	212	
7	6	0	269	276	
7	6	1	196	172	
7	6	2	236	227	
7	6	3	118	114	
7	7	0	127	126	
7	7	1	210	203	
7	7	2	254	247	
7	7	3	125	134	
8	0	0	205	178	
8	0	1	185	179	
8	0	2	542	590	
8	0	3	302	337	
8	0	4	91	87	
8	0	5	58	60	
8	1	0	26	27	*
8	1	1	116	98	
8	1	2	81	29	*
8	1	3	49	64	
8	1	4	16	28	*
8	2	0	265	278	
8	2	1	233	243	
8	2	2	211	205	
8	2	3	196	187	
8	2	4	160	144	
8	2	5	72	64	
8	3	0	257	251	
8	3	1	451	434	
8	3	2	218	212	
8	3	3	308	288	
8	3	4	127	137	
8	3	5	106	136	
8	4	0	396	380	
8	4	1	198	206	
8	4	2	89	80	
8	4	3	182	181	
8	4	4	203	173	
8	5	0	142	129	
8	5	1	209	198	
8	5	2	136	125	
8	5	3	135	136	
8	6	0	52	50	
8	6	1	243	235	
8	6	2	282	279	
8	6	3	170	162	
8	7	0	35	26	
8	7	1	126	107	
8	7	2	86	38	*
8	7	3	78	75	
8	8	0	496	474	
8	8	1	187	195	
8	8	2	132	137	
8	8	3	52	53	*
9	0	1	49	28	*
9	0	2	81	11	*
9	0	3	66	22	*
9	0	4	6	14	*
9	0	5	2	16	*
9	1	0	78	56	
9	1	1	179	186	
9	1	2	433	423	
9	1	3	202	221	
9	1	4	32	53	
9	2	0	229	228	
9	2	1	205	184	
9	2	2	205	202	
9	2	3	160	132	
9	2	4	140	145	
9	3	0	271	253	
9	3	1	228	236	
9	3	2	161	156	
9	3	3	82	78	
9	4	0	130	127	
9	3	4	49	148	*
9	4	1	74	64	
9	4	2	107	104	
9	4	3	62	62	
9	4	4	53	57	
9	5	0	109	97	
9	5	1	206	202	
9	5	2	241	225	
9	5	3	169	178	
9	6	0	121	104	
9	6	1	237	211	
9	6	2	84	108	*
9	6	3	152	152	
9	7	0	282	272	
9	7	1	150	156	
9	7	2	76	42	*
9	7	3	51	73	*
9	8	0	19	21	
9	8	1	43	19	*
9	8	2	64	18	*
9	8	3	49	11	*
9	9	0	315	340	
9	9	1	119	136	
9	9	2	64	91	
9	9	3	49	25	*
10	0	0	25	12	*
10	0	1	173	180	
10	0	2	309	311	
10	0	3	140	142	
10	0	4	4	4	*
10	1	0	116	120	
10	1	1	93	84	
10	1	2	101	102	
10	1	3	46	58	
10	1	4	99	65	*
10	2	0	324	324	
10	2	1	352	354	
10	2	2	77	51	*
10	2	3	212	223	
10	2	4	168	145	
10	3	0	144	129	
10	3	1	153	127	
10	3	2	124	111	
10	3	3	105	118	
10	3	4	60	73	
10	4	0	188	178	
10	4	1	207	207	
10	4	2	144	132	
10	4	3	125	123	
10	5	0	195	201	
10	5	1	51	92	*
10	6	0	21	16	*
10	5	2	159	168	
10	5	3	66	89	
10	6	1	202	201	
10	6	2	213	229	
10	6	3	167	180	
10	7	0	18	5	*
10	7	1	69	59	
10	7	2	60	22	*
10	7	3	49	49	*
10	8	0	128	130	
10	8	1	165	157	
10	8	2	59	81	*
11	0	1	314	299	
11	0	2	69	74	*
11	0	3	187	212	
11	1	0	281	274	
11	1	1	172	179	
11	1	2	82	66	
11	1	3	74	90	
11	2	0	16	9	
11	2	1	46	20	*
11	2	2	29	28	
11	2	3	42	41	
11	3	0	375	382	
11	3	1	156	162	
11	3	2	63	69	
11	3	3	52	64	
11	4	0	190	180	
11	4	1	40	21	
11	4	2	148	152	
11	4	3	41	42	*
11	5	0	25	26	
11	5	1	113	114	
11	5	2	175	198	
11	6	0	16	17	*
11	6	1	38	10	*
11	6	2	51	12	*
11	7	0	58	56	
11	7	1	142	157	
12	0	0	187	194	
12	0	1	128	136	
12	0	2	73	61	
12	0	3	19	71	*
12	1	0	95	99	
12	1	1	152	153	
12	1	2	68	82	
12	2	0	200	203	
12	2	1	133	147	
12	2	2	64	43	
12	3	0	71	82	
12	3	1	21	14	
12	3	2	52	68	
12	4	0	158	160	
12	4	1	187	214	
12	4	2	71	87	
12	5	0	13	16	*
12	5	1	30	36	*
13	0	1	89	86	
13	1	0	108	97	
13	1	1	137	140	
13	2	0	211	213	
13	2	1	25	16	*
13	3	0	64	57	

The final parameters are listed in Table 1 together with their standard deviations. A comparison of observed and calculated structure factors is given in Table 2, the figures for non-observed reflections being those used in the least-squares calculations.

DISCUSSION

The structure as viewed down the *c*-axis is illustrated in Fig. 1, and Table 3 gives interatomic distances and bond angles. The bond lengths and angles are also shown in Fig. 2.

The magnitudes and direction cosines of the principal axes of the ellipsoids of vibration as calculated from the thermal parameters are listed in Table 4. The anisotropy of both ions appear to be mainly due to translational lattice

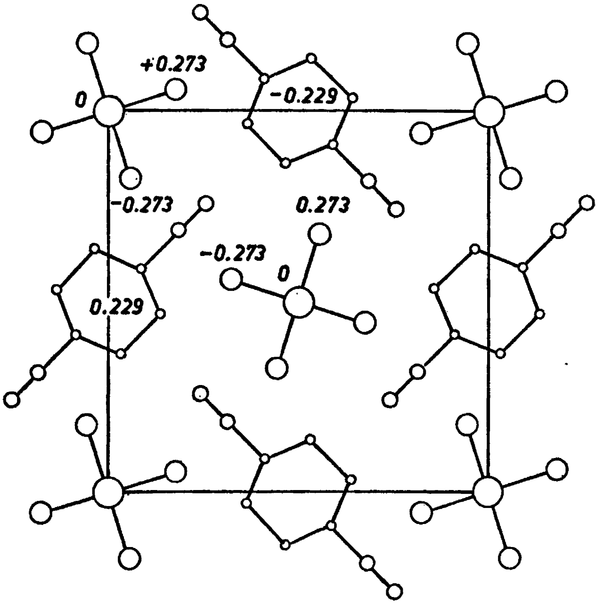

Fig. 1. The structure as viewed down the *c*-axis; *z*-parameters are given for the zinc and chlorine atoms and for the plane of the tetrazonium ion.

Table 3. Interatomic distances (Å) and bond angles (°). (Standard deviations in parenthesis).

N(1)–N(2)	1.09(0.012)	C(2)–C(1)–C(6)	128.2(1.2)
N(2)–C(1)	1.42(0.012)	C(1)–C(2)–C(3)	115.9(0.8)
C(1)–C(2)	1.37(0.013)	Cl–Zn–Cl′	117.0(0.2)
C(2)–C(3)	1.42(0.017)	Cl–Zn–Cl″	105.8(0.2)
Zn–Cl	2.283(0.002)		
C(1)–C(4)	2.62(0.018)		
C(2)–C(5)	2.85(0.017)		

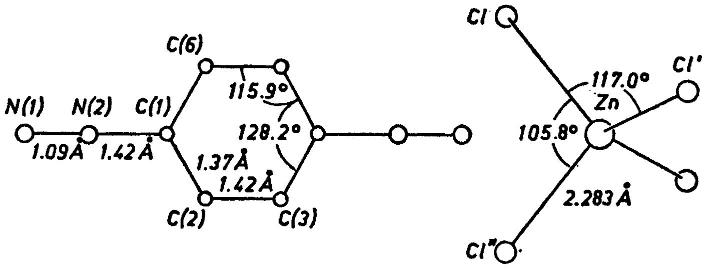

Fig. 2. Interatomic distances in the benzenetetrazonium and tetrachlorozincate ions.

Table 4. Magnitudes and direction cosines of the principal axes of the ellipsoids of vibration.

Atom	B	Direction cosines		
Zn	3.48	0.000	0.000	1.000
	2.05	1.000	0.000	0.000
	2.06	0.000	1.000	0.000
Cl	3.06	0.213	0.239	0.947
	2.06	−0.972	0.153	0.180
	1.64	−0.103	−0.959	0.265
N(1)	4.82	−0.308	0.308	0.900
	2.77	−0.707	−0.707	0.000
	1.81	−0.636	0.636	−0.436
N(2)	3.32	01326	−0.326	−0.887
	1.76	0.627	−0.627	0.461
	1.33	0.707	0.707	0.000
C(1)	2.92	0.188	−0.188	0.964
	2.12	0.707	0.707	0.000
	1.35	0.682	−0.682	−0.265
C(2)	2.93	0.092	0.243	0.966
	1.71	0.598	0.762	−0.249
	1.30	0.796	−0.600	0.075

vibrations, the maximum amplitudes running parallel to the c-axis. The amplitudes of the atoms in the tetrazonium ion decrease in the order N(1), N(2), C, which might indicate an oscillation of the ion about an axis through the centre of the ion normal to the C(1)—C(4) direction. The differences are very small, however, and a librational analysis gave no significant corrections of the interatomic distances.

The zinc atom is nearly tetrahedrally surrounded by chlorine atoms, the two different Cl—Zn—Cl angles being 105.8° and 117.0°, both with an estimated standard deviation of 0.2°. The Zn—Cl distance is 2.238 Å (e.s.d. 0.002 Å), in close agreement with the results from other structural investigations of the tetrachlorozincate ion.[2,9]

The tetrazonium ion is planar within the accuracy of the analysis; the largest deviation of any atom from the best plane is about twice the standard deviation of the atomic position. Assuming planarity the ion has *mmm* symmetry, and the C—N—N arrangement is linear.

The N—N bond length of 1.09 ± 0.01 Å * is the same as that found in benzenediazonium chloride[1] (1.097 ± 0.006 Å). No reference to the length of a bond between an sp^2-hybridized carbon and an sp-hybridized nitrogen atom is known to the authors. If, however, the shortening of the $C(sp^2)$—$N(sp)$ relative to the $C(sp^2)$—$N(sp^3)$ bond length is the same as for the correspondingly hybridized C—C bonds, a bond length of about 1.37 Å would have been expected.[10] The C(1)—N(2) bond length seems accordingly too long for a pure hybridization of this type.

The effect of the diazonium groups on the benzene ring is shown by the significant shortening of the C(1)—C(4) diagonal which is found to be 2.62 ± 0.02 Å. The same feature although less conspicuous was observed in benzene diazonium chloride (2.69 Å) and in o-$CH_3{\cdot}C_6H_4N_2{\cdot}FeCl_4$.[3] The C(2)—C(1)—C(6) angle is 128.2 ± 1.2°, as compared to 124.8 ± 0.6° in benzenediazonium chloride.

A qualitative description of the distortion of the benzene ring is possible by assuming a decrease in *p* character of the C(1) orbitals along the C(1)—C(2) and C(1)—C(6) bonds and a corresponding increase in the *p* character along the C(1)—N(2) bond. This would open the angle C(2)—C(1)—C(6), and increase the C(1)—N(2) bond length. It would also tend to make the C(1)—C(2) bond shorter than the C(2)—C(3) bond, as indicated by the present analysis.

The reason for this observed "anti-quinoid" geometry of the ring is thought to be the electrophilic character of the substituent. The same tendency was found in benzenediazonium chloride,[1] but since only one diazonium group is present, the effect is less marked. Benzonitrile[11] has a similar ring geometry; the C(2)—C(1)—C(6) angle is 122.5° and the C(1)—C≡ bond is 0.03 Å longer than the $C(sp^2)$—$C(sp)$ single bond.

The coordination of chloride atoms around the N_2^+ group is very similar to that observed in the benzenediazonium chloride. N_2^+ is surrounded by *four* chlorine atoms in a plane normal to the N—N axis in an approximately square arrangement. The non-equivalent distances from chlorine atoms to the "inner" nitrogen atom are 3.26 Å and 3.32 Å, and to the "outer" nitrogen atom 3.43 Å and 3.44 Å. There are further two N—Cl contacts of 3.27 Å to the outer nitrogen atom. Since the normal van der Waals' separation between nitrogen and chlorine is about 3.3 Å, it is difficult to draw any conclusions as to the charge distribution in the diazonium group from the geometrical arrangement.

In addition to the Cl—N contacts there is a short intermolecular separation between chlorine and hydrogen atoms. The distance is somewhat uncertain since the position of the hydrogen atom is not derived from the structure determination. Assuming a normal geometry, however, the H—Cl distance is about 2.6 Å, about 0.4 Å shorter than the sum of the van der Waals' radii. The C—H···Cl arrangement is not far from linear, and we conclude that a

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* the ± values indicate estimated standard deviations.

hydrogen bond is present and that this is facilitated by the electron-withdrawing properties of the diazonium groups.

The coordination polyhedron around the chlorine atom is a distorted trigonal bipyramid, the equatorial bonds being those to zinc and N_2^+ groups and the axial being the hydrogen bond and the 3.27 Å contact to an outer nitrogen atom.

REFERENCES

1. Rømming, Chr. *Acta Chem. Scand.* **17** (1963) 1444.
2. Polynova, T. N., Bokii, N. G. and Porai-Koshits, M. A. *Zh. Strukt. Khim.* **6** (1965) 878.
3. Polynova, T. N. and Nesterova, J. M. *Acta Cryst.* **21** (1966) A149; (IUCr 7th. Intern. Congr. and Symp. Moscow 1966).
4. Schoutissen, H. A. J. *J. Am. Chem. Soc.* **55** (1933) 4535.
5. Zachariassen, W. H. *Acta Cryst.* **16** (1963) 1139.
6. Åsbrink, S. and Werner, P. E. *Acta Cryst.* **20** (1966) 407.
7. Hamilton, W. C. *Acta Cryst.* **8** (1955) 185.
8. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
9. Morosin, B. and Lingafelter, E. C. *Acta Cryst.* **12** (1959) 611.
10. Bastiansen, O. and Trætteberg, M. *Tetrahedron* **17** (1962) 149.
11. Bak, B., Christensen, D., Dixon, W. B., Hansen-Nygaard, L. and Rastrup-Andersen, J. *J. Chem. Phys.* **37** (1962) 2027.

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