The Structure of Benzene Diazonium Chloride

CHR. RÖMMING

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

The structure of benzenediazonium chloride has been determined by X-ray methods. The crystals are orthorhombic, space group $C222_1$ with unit cell dimensions: $a = 15.152$ Å, $b = 4.928$ Å, $c = 9.044$ Å. The shortest Cl^- to N distance is 3.225 Å, and the bond lengths in the benzenediazonium ion were found to be as follows: $N(2)-N(1) = 1.097$ Å, $N(1)-C(1) = 1.385$ Å, $C(1)-C(2) = 1.374$ Å, $C(2)-C(3) = 1.383$ Å, $C(3)-C(4) = 1.376$ Å. Some of the valence angles in the ring deviate significantly from 120°. The $N(2)-N(1)-C(1)$ arrangement is strictly linear.

A preliminary X-ray examination of benzenediazonium chloride $C_6H_5N_2Cl$, demonstrated[1] the crystals to be of ionic nature and to contain benzenediazonium ions and chloride ions. The space group requires the $N(2)-N(1)-C(1)----C(4)$ atoms to be situated on a two-fold axis of symmetry and it was thus possible to determine the distances between these atoms from one projection normal to this axis. The N—N and N—C bonds were found to be of about the expected length; the $C(1)---C(4)$ distance across the ring, however, appeared to be about 0.1 Å shorter than in benzene, and this difference could not be ascribed to inaccuracy of the determination. A distortion of the carbon ring relative to the benzene configuration was anticipated, but in order to determine the structure of the compound with higher precision the parameters were subjected to a refinement based on three dimensional X-ray data.

EXPERIMENTAL

Benzenediazonium chloride was prepared (Knoevenagel[2]) by the action of amyl nitrite on aniline hydrochloride dissolved in glacial acetic acid at temperatures below 5°C followed by precipitation of the diazonium salt by ether. It was found, however, that the crystals slowly precipitated by this method contained one mole of acetic acid per mole of the salt. The compound was therefore redissolved in ethyl alcohol and needle-formed crystals of the pure benzenediazonium chloride were obtained by precipitation at low temperatures by diffusion of ether into the solution.

The dimensions of the orthorhombic unit cell were determined from Guinier diagrams taken at room temperature, the space group from oscillation photographs of a crystal

rotating about the b-axis and from h0l, h1k and h2l Weissenberg films and hk0 and 0kl precession diagrams.

The intensities of the hkl-reflections were recorded on photographs taken on an integrating Weissenberg camera with a crystal rotating about the b-axis; equi-inclination photographs of layers with k up to 4 were taken using the multiple film technique. To avoid large inclination angles MoKα-radiation (Zr-filtered) was used. Owing to the thermal damping only few reflections outside the limiting sphere in the reciprocal lattice corresponding to the CuKα wave-length were obtained. In order to bring the intensities from the various layers to a common scale intensity data of the 0kl and hk0-zones were collected by means of precession photographs. The dimensions of the crystal used in the experimental work were about $0.1 \times 0.1 \times 0.2$ mm³. These were kept in sealed-off Pyrex capillary tubes having a wall thickness less than 0.01 mm. The intensities were measured microphotometrically except for the weakest reflections, the intensities of which were estimated visually by comparison with a calibrated scale.

Of the 442 reflections obtainable within the CuKα-sphere 302 were actually measured and furthermore 13 reflections having higher sin Θ/λ-values were obtained.

The atomic form factors used during the refinement calculations were taken from the paper by Berghuis et al. [3] The nitrogen atoms were both given the atomic form factor of a neutral nitrogen atom.

CRYSTAL DATA

Benzenediazonium chloride, M = 140.58
Orthorhombic
$a = 15.152 \pm 0.006$ Å, $b = 4.928 \pm 0.002$ Å, $c = 9.044 \pm 0.003$ Å.
Volume of unit cell: 675.3 Å³.
Density, calculated assuming *four* formula units per unit cell: 1.383 g cm⁻¹.
Absent spectra: hkl when $h + k = 2n + 1$, 00l when $l = 2n + 1$.
Space group: $C222_1 - D_2^5$.

TWO-DIMENSIONAL ANALYSIS

In the three projections along the orthorhombic axes the normal procedure for refinements was followed. Approximate coordinates were obtained from Patterson projections and Fourier refinements were then performed until no change of sign of the structure factors occurred. Two-dimensional least squares refinements were continued until the parameter shifts were appreciably less than the probable error in the coordinates.

The projection along the b-axis [1] was well resolved, and the refinement of the x and z parameters resulted in an R-factor of 5.5 %. Hydrogen atoms with assumed positions were included in the calculations. It was found that the chloride ions are situated on two-fold axes parallel to b and the benzene diazonium ions on two-fold axes along a. In the projections along the a-axis the chloride ion only was resolved while, owing to symmetry requirements, two nitrogen and two of the carbon atoms on the two-fold axis of the diazonium ion overlap perfectly.

Since the pair of carbon atoms C(2) and C(3) of the benzene ring must also have very nearly the same y and z parameters this projection could be refined independently of the others. The R-factor arrived at was 10.0 %. More serious overlapping occurred in the projection along the c-axis. Using the x parameters from the [010]-projection for the nitrogen atoms, however,

Table 1. Parameters obtained from the two dimensional analysis. Assumed values in parentheses.

		[010]	[100]	[001]
Cl⁻	$x = 0$ y $z = 1/4$		0.05	0.06
N(1)	x $y = 1/2$ $z = 1/2$	0.038		(0.038)
N(2)	x $y = 1/2$ $z = 1/2$	−0.035		(−0.035)
C(1)	x $y = 1/2$ $z = 1/2$	0.132		0.136
C(2)	x y z	0.173 0.405	0.66 0.408	0.171 0.69
C(3)	x y z	0.265 0.406	0.66 0.408	0.257 0.66
C(4)	x $y = 1/2$ $z = 1/2$	0.310		0.307

the refinements of the other atomic parameters by the method of least squares brought the R-factor down to 8.9 %.

The parameters arrived at in the three projections are listed in Table 1; it may be seen by comparison with Table 2 that the x and z parameters differ very little from the ones obtained later in the three-dimensional analysis.

THREE-DIMENSIONAL REFINEMENT

The mean values of the parameters given in Table 1 and parameters assumed for the hydrogen atoms were used for calculation of the structure factors corresponding to the three-dimensional data set. After adjustments of the scale factors for the various layer line data the unreliability factor was 0.11 apart from non-observed reflections. The parameters were then further refined employing a three-dimensional (block diagonal) least squares refinement program prepared by J. S. Rollett for the Ferranti MERCURY computer. The 315 observed reflections were included in the calculations where the 11 positional and 32 (anisotropic) vibrational parameters of the heavier atoms were refined; the hydrogen parameters were kept constant during these calculations assuming isotropic thermal vibrations with $B = 4$ $Å^{-2}$, which is slightly above the corresponding values for the carbon atoms to which they are bonded.

Table 2. Final positional parameters given as fractions of the cell edges.

	x	y	z
Cl⁻	0	0.0450	¹/₄
N(1)	0.0386	½	½
N(2)	−0.0339	½	½
C(1)	0.1300	½	½
C(2)	0.1720	0.673	0.4037
C(3)	0.2633	0.678	0.4034
C(4)	0.3075	½	½
H(2)	(0.136)	(0.803)	(0.329)
H(3)	(0.299)	(0.803)	(0.329)
H(4)	(0.379)	½	½

After a couple of refinement cycles the R-factor had decreased to 0.07. At this stage new hydrogen parameters were calculated to give a carbon to hydrogen bond distance of 1.09 Å, and the layer line scale factors were also adjusted. The refinements then proceeded until only negligible parameter shifts occurred; the R-factor was then 0.06.

The final positional parameters are listed in Table 2, and a comparison of the observed and calculated structure factors is given in Table 3.

The coefficients in the expression for the corrections for the anisotropic thermal effects, exp $(- \sum_i \sum_j B_{ij} h_i h_j)$, arrived at in the least squares refinement were analysed [4] in order to determine the principal axes of the vibrational ellipsoids. The results are listed in Table 4; for each atom is given the B_{ij}, the mean $\bar{B}$-value (geometrical mean of the B-values in the direction of the principal axes), the root mean square amplitude of vibration in the principal directions and angles between these directions and the crystallographic axes. The anisotropy of the thermal vibrations was not found large enough for any of the atoms to justify corrections in the co-ordinates and thus in the interatomic distances.

The chloride ions vibrate very nearly isotropically. The benzenediazonium ion as a whole has its largest amplitude of vibration in the plane of the benzene ring, normal to its twofold axis, but there may also be a small oscillation of the ion about this axis.

As the output from the least squares computations did not allow an evaluation of the standard deviation in the co-ordinates, the standard deviations were estimated using the formula[5] referring to a refinement by Fourier methods. The electron densities and curvature constants were obtained from a three-dimensional Fourier map, and since the structure is noncentrosymmetrical, an n-shift factor (1.7) was applied to the standard deviations evaluated from the formula. The estimated standard deviations of the atomic co-ordinates were as follows:

$$\text{Cl}^- \ : \sigma(y) = 0.001 \text{ Å}$$
$$\text{N(1)} \ : \sigma(x) = 0.005 \text{ Å}$$
$$\text{N(2)} \ : \sigma(x) = 0.004 \text{ Å}$$
$$\text{C(1)} \ : \sigma(x) = 0.007 \text{ Å}$$
$$\text{C(2) and C(3)} \ : \sigma(x) = \sigma(z) = 0.007 \text{ Å}$$
$$\text{C(4)} \ : \sigma(x) = 0.008 \text{ Å}$$

Table 3. Observed and calculated structure factors.

h	k	l	F_o	F_c	$a_c°$	h	k	l	F_o	F_c	$a_c°$
0	0	2	48.8	48.0	0	10	0	6	16.6	15.2	180
		4	56.4	54.7	0			7	10.3	9.4	270
		6	19.1	18.5	180			8	9.7	9.3	0
		8	33.4	33.4	0	12	0	0	17.2	16.4	0
		10	4.6	3.5	0			1	< 5.4	0.5	270
		12	11.5	13.5	0			2	31.5	33.5	180
2	0	0	20.2	21.1	0			3	10.7	9.3	90
		1	28.1	29.5	270			4	< 5.4	4.9	180
		2	51.3	48.0	180			5	15.6	13.9	90
		3	< 3.6	1.6	90			6	27.6	31.6	180
		4	78.6	78.0	0			7	7.4	6.1	90
		5	8.4	6.4	90			8	3.5	4.8	0
		6	< 5.4	3.8	180	14	0	0	< 5.4	0.8	180
		7	< 5.4	0.3	270			1	< 5.4	4.3	90
		8	19.5	20.0	0			2	27.1	28.0	180
		9	< 4.8	4.6	270			3	< 5.4	2.0	90
		10	14.0	15.4	180			4	12.6	14.2	0
4	0	0	75.6	80.8	0			5	< 4.5	1.0	90
		1	< 3.3	0.7	270			6	11.2	10.8	180
		2	36.2	33.8	180	16	0	0	13.8	15.4	0
		3	13.4	13.5	270			1	< 4.5	2.2	90
		4	31.6	31.4	0			2	13.0	12.9	180
		5	16.6	15.9	270			3	< 3.9	0.4	90
		6	28.3	27.7	180			4	10.7	10.7	0
		7	5.3	6.6	270			5	< 2.7	0.3	270
		8	17.4	17.8	0			6	7.2	8.9	180
		9	< 4.5	0.1	90	18	0	0	7.5	7.1	0
		10	8.4	9.7	180			1	< 2.7	0.5	270
6	0	0	65.3	65.7	0			2	12.8	15.3	180
		1	29.7	29.5	90	1	1	2	100.0	108.1	210.4
		2	23.3	24.4	180			3	30.2	28.8	39.0
		3	9.9	10.7	90			4	23.4	21.0	301.4
		4	39.1	37.1	0			5	6.2	6.3	182.3
		5	7.3	7.9	90			6	34.9	36.6	168.5
		6	16.9	17.6	180			7	< 6.4	6.7	210.4
		7	< 5.8	4.7	90			8	13.1	12.9	48.8
		8	18.9	18.5	0			9	8.0	9.2	118.3
		9	< 4.8	3.8	90			10	15.5	15.9	174.6
		10	7.1	7.6	180	3	1	0	27.6	27.4	0
8	0	0	30.0	30.1	0			1	28.3	27.2	195.4
		1	25.9	24.8	270			2	71.8	74.7	161.2
		2	34.6	34.9	180			3	10.3	8.7	105.2
		3	< 4.8	1.7	90			4	16.1	14.4	47.2
		4	23.3	22.8	0			5	14.9	12.8	126.3
		5	20.7	20.3	90			6	33.8	35.2	186.9
		6	20.7	20.3	180			7	12.6	11.8	17.4
		7	< 5.4	1.6	90			8	13.9	13.2	335.4
		8	12.0	13.9	0			10	11.0	11.1	184.9
		9	4.4	4.7	270	5	1	0	43.8	43.4	0
		10	7.8	9.1	180			1	17.9	16.6	222.5
10	0	0	10.7	8.6	0			2	33.0	33.1	179.3
		1	10.6	10.3	90			3	18.4	18.0	321.7
		2	36.0	35.6	180			4	34.3	33.8	357.8
		3	11.7	11.2	270			5	7.9	8.6	226.5
		4	20.7	22.6	0			6	18.0	17.7	177.5
		5	19.8	19.8	270			7	< 6.7	4.4	313.7

h	k	l	F_o	F_c	$a_c{}°$	h	k	l	F_o	F_c	$a_c{}°$
5	1	8	16.4	17.1	2.4	2	2	4	25.7	26.4	11.3
		0	13.4	14.2	0			5	15.0	15.6	205.4
		1	< 4.8	2.7	67.9			6	17.7	18.7	186.3
		2	45.6	45.5	183.3			7	4.9	3.6	269.0
7	1	3	19.1	18.6	5.2			8	14.9	15.2	350.2
		4	18.7	20.0	357.8			9	11.8	11.1	184.1
		5	8.1	5.7	171.7	4	2	0	30.5	32.0	0
		6	21.8	21.9	177.7			1	29.5	29.1	208.7
		7	< 7.0	1.6	5.4			2	26.7	27.5	198.2
		8	10.2	9.4	8.1			3	11.6	10.8	322.5
9	1	0	40.2	42.5	0			4	25.7	26.6	352.5
		1	20.2	19.3	175.3			5	14.2	12.9	184.9
		2	19.0	18.7	192.4			6	14.2	13.8	172.5
		3	8.1	9.5	187.0			7	13.2	11.6	348.0
		4	19.1	18.1	354.0			8	13.7	12.8	11.5
		5	8.9	7.8	186.7			9	8.5	6.5	208.8
		6	19.3	20.2	176.9	6	2	0	33.7	33.5	0
		7	10.0	10.9	3.2			1	20.1	19.4	148.3
		8	13.2	13.2	6.1			2	14.6	15.6	188.7
11	1	0	32.4	34.4	0			3	17.1	17.3	43.4
		1	< 6.2	0.8	348.9			4	26.9	28.4	353.2
		2	12.2	10.6	115.5			5	14.7	15.1	148.2
		3	17.8	18.2	19.3			6	12.2	10.9	181.5
		4	34.1	38.2	9.2			7	10.7	10.0	32.9
		5	< 7.1	8.7	116.2			8	14.1	13.4	2.1
		6	< 7.4	3.1	269.6	8	2	0	18.5	19.8	0
		7	< 7.9	4.5	132.5			1	14.8	15.0	162.6
		8	15.8	17.0	346.0			2	24.4	25.7	155.7
13	1	0	26.3	28.8	0			3	13.7	13.1	338.6
		1	8.1	8.2	193.5			4	17.3	17.2	22.1
		2	12.0	13.0	224.0			5	14.0	12.0	217.2
		3	< 7.1	7.9	268.6			6	15.0	15.0	193.9
		4	18.8	19.3	343.8			7	11.2	9.0	331.0
		5	8.8	9.9	238.6			8	12.0	11.2	336.5
		6	< 8.0	9.8	159.3	10	2	0	17.1	17.5	0
		7	< 8.3	6.4	315.1			1	15.3	15.6	241.6
		8	11.8	12.3	216.5			2	22.2	24.3	210.7
15	1	0	21.2	20.5	0			3	17.6	17.6	343.6
		1	< 7.5	8.6	237.4			4	12.8	11.5	325.4
		2	< 7.7	9.2	153.6			5	7.6	7.9	171.7
		3	< 7.8	4.9	306.5			6	16.4	17.4	167.4
		4	15.3	16.2	8.3			7	< 5.8	4.7	342.9
17	1	0	15.6	14.3	0			8	9.3	8.7	38.2
19	1	0	12.0	10.7	0	12	2	0	7.2	5.1	180
0	2	0	60.6	62.0	0			1	17.0	18.5	144.3
		1	38.9	42.0	180			2	28.9	31.8	167.7
		2	10.0	10.0	0			3	< 5.9	5.9	69.3
		3	12.0	12.5	180			4	7.8	5.8	34.3
		4	65.5	67.2	0			5	< 6.3	6.2	167.0
		5	18.4	18.8	180			6	15.3	15.2	191.1
		6	9.1	8.8	0			7	10.8	11.1	7.0
		7	16.7	18.0	0	14	2	0	11.1	9.7	0
		8	22.2	24.9	0			1	< 5.1	4.2	154.7
		9	7.6	4.0	180			2	16.2	16.9	185.6
2	2	0	67.6	71.2	0			3	13.5	13.4	7.6
		1	8.3	8.1	154.9			4	< 5.9	3.2	345.1
		2	14.0	14.4	139.8			5	< 6.1	5.7	156.2
		3	35.1	35.9	351.1			6	15.7	14.0	179.7

h	k	l	F_o	F_c	$a_c°$	h	k	l	F_o	F_c	$a_c°$
16	2	0	9.5	9.8	0	11	3	3	9.1	9.2	6.1
		1	< 6.0	6.8	178.5			4	13.4	12.9	357.4
		2	11.0	9.2	184.4			5	12.0	11.9	192.5
18	2	0	< 6.4	0.1	180			6	5.3	4.9	185.4
		1	< 6.5	6.2	193.4			7	< 5.2	5.4	2.0
		2	14.9	13.6	182.6			8	8.2	10.4	2.4
1	3	1	19.4	21.3	195.4	13	3	0	9.6	9.8	0
		2	32.0	32.1	177.5			1	15.0	15.0	224.8
		3	25.2	24.2	32.5			2	4.9	5.4	174.1
		4	< 3.1	0.7	80.4			3	7.1	8.6	345.7
		5	24.3	24.3	119.9			4	14.5	13.4	5.9
		6	20.9	21.9	178.7			5	7.8	8.4	166.5
		7	16.0	16.5	33.6	15	3	0	12.7	10.3	0
		8	< 4.6	3.3	339.6			1	7.5	8.1	186.2
		9	5.3	5.7	188.7			2	< 5.0	3.8	178.5
		10	5.7	7.9	191.9			3	7.7	8.2	330.0
3	3	0	< 3.0	3.1	180			4	7.9	8.7	1.2
		1	23.6	22.5	146.2			5	7.0	8.5	213.2
		2	32.2	30.6	179.9	17	3	0	8.1	7.9	0
		3	21.2	20.1	359.6			1	8.1	7.9	147.5
		4	11.3	11.0	354.7	19	3	0	8.7	8.8	0
		5	13.5	13.8	202.5	0	4	0	16.1	20.6	0
		6	11.8	12.3	186.0			1	11.0	13.1	180
		7	12.0	11.6	357.1			2	6.0	6.7	0
		8	5.0	4.7	0.9			3	24.0	24.6	0
		9	7.6	7.6	153.2			4	24.5	24.4	0
		10	8.1	8.3	176.6			5	13.6	14.4	180
5	3	0	23.3	23.0	0			6	6.4	6.5	0
		1	20.3	19.3	201.0			7	< 4.4	2.3	0
		2	12.2	12.6	183.3			8	9.2	9.1	0
		3	16.1	16.9	346.9			9	12.3	12.3	180
		4	13.8	14.0	5.7	2	4	0	15.2	17.5	0
		5	14.6	13.3	192.2			1	19.5	22.9	182.2
		6	9.3	9.3	169.5			2	4.4	4.4	230.9
		7	11.5	11.2	347.4			3	6.7	7.2	341.3
		8	8.8	9.2	5.3			4	7.8	7.3	344.8
		9	7.7	7.0	193.4			5	16.4	16.6	189.8
		10	5.9	3.4	182.1			6	4.0	5.0	161.7
7	3	0	14.0	14.1	0			7	12.6	12.4	351.4
		1	16.7	17.0	180			8	9.3	7.2	17.2
		2	17.5	17.3	175.7	4	4	0	7.3	6.9	0
		3	16.4	14.8	3.5			1	13.5	16.0	196.9
		4	< 3.8	3.0	10.1			2	7.8	7.8	154.5
		5	13.0	12.3	171.5			3	17.8	17.5	350.5
		6	16.5	17.4	181.4			4	10.2	9.0	10.1
		7	9.2	9.6	5.2			5	13.0	12.9	187.1
9	3	0	5.5	2.5	0			6	6.0	4.6	195.8
		1	14.2	14.2	188.9			7	10.4	8.1	350.2
		2	15.1	14.8	180.6			8	< 4.9	3.2	335.3
		3	13.7	13.7	4.0			9	7.4	7.9	188.9
		4	17.5	18.6	2.0	6	4	0	11.3	11.8	0
		5	12.9	10.6	16.56			1	15.0	16.3	161.0
		6	4.9	1.5	160.0			2	< 3.3	3.5	179.4
		7	7.4	7.8	8.5			3	14.8	15.4	20.2
		8	5.6	5.9	359.8			4	9.7	8.6	3.0
11	3	0	33.0	33.1	0			5	12.2	13.2	159.2
		1	16.1	15.9	143.2			6	< 4.4	2.7	205.3
		2	6.4	4.3	357.0			7	9.1	8.2	20.0

h	k	l	F_o	F_c	a_c°	h	k	l	F_o	F_c	a_c°
8	4	0	5.0	5.3	0	12	4	0	6.3	5.0	180
		1	13.2	14.0	179.1			1	7.9	8.5	143.6
		2	9.6	8.7	217.5			2	12.5	12.9	197.5
		3	12.6	12.9	348.5			3	13.8	14.7	9.0
		4	8.1	6.8	326.4			4	< 4.8	2.6	258.3
		5	11.7	10.8	197.6			5	6.2	5.9	169.2
		6	< 4.6	4.6	166.3			6	5.2	7.1	178.5
		7	9.4	8.1	351.1	14	4	0	6.9	2.3	0
10	4	0	5.6	5.1	0			1	10.8	10.0	174.5
		1	14.0	14.9	204.4			2	8.7	6.4	178.2
		2	9.9	9.6	140.7	0	6	0	7.7	8.4	0
		3	8.3	9.2	344.9			1	7.7	9.3	180
		4	4.4	4.3	69.1			2	9.3	7.7	0
		5	9.1	8.7	184.3						

DISCUSSION OF THE STRUCTURE

The crystals are built up of chloride and benzenediazonium ions in layers normal to the a-axis. The chloride ions lie on two-fold axes parallel to b in the planes $x = 0$ and $x = \frac{1}{2}$; the two-fold axis of the benzenediazonium ion runs parallel to the a-axis. Planes containing chloride ions bisect the N-N bond of the diazonium ions. In a row of benzenediazonium ions along c the N(2)—N(1)—C(1)————C(4) axes are pointing alternately along the positive

Table 4. Thermal vibration data.

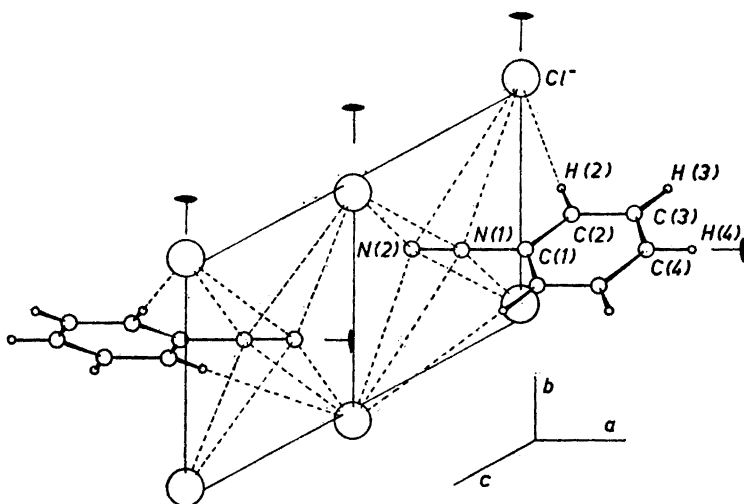| Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}	B Å	$\sqrt{\overline{u^2}}$ Å	a_1°	a_2°	a_3°
Cl⁻	0.00286	0.02989	0.00873	0	−0.00012	0	2.79	0.19 0.19 0.18	90 105 15	0 90 90	90 15 105
N(1)	0.00270	0.04327	0.01235	−0.00709	0	0	3.37	0.26 0.19 0.18	90 90 0	137 47 90	47 43 90
N(2)	0.00284	0.05075	0.01730	−0.01276	0	0	3.90	0.31 0.20 0.18	90 90 0	130 40 90	40 50 90
C(1)	0.00189	0.03508	0.00940	−0.00480	0	0	2.89	0.23 0.17 0.15	90 90 0	141 51 90	51 39 90
C(2)	0.00280	0.05159	0.01162	0.00144	−0.00020	−0.00027	3.66	0.25 0.22 0.18	90 91 5	12 102 89	78 13 85
C(3)	0.00361	0.05170	0.01311	0.00660	0.00070	0.00034	4.04	0.27 0.21 0.20	85 54 143	37 123 107	54 53 57
C(4)	0.00309	0.04412	0.01415	−0.00226	0	0	3.82	0.25 0.23 0.19	90 90 0	124 34 90	34 56 90

Fig. 1. The layer of chloride and benzenediazonium ions.

and the negative a-axis. The arrangement is visualized in Fig. 1 where a part of an ionic layer is shown. The layers are separated by a vector $\frac{1}{2}$ ($a + b$); chlorine atoms of one layer lie on approximately the same y level as the H(4)-atoms of the next layer, the Cl^{-}—H(4) separation being 2.92 Å. This is close to the van der Waals' radius sum for hydrogen and chlorine atoms and the length of the a-axis is believed to be determined mainly by the interaction between these atoms.

Every $(N \equiv N-)^{+}$ group is surrounded by four chloride ions in a planar arrangement normal to the N—N-axis, two of them are at a distance of 3.184 Å and two at a distance of 3.511 Å from this axis. The distances from the former chloride ions, the connecting line of which runs nearly normal to the plane of the benzene ring, to the (N2) and N(1) are 3.225 Å and 3.237 Å, respectively. The corresponding distances from the other set of chloride ions to the N(2) and N(1) atoms are 3.548 Å and 3.559 Å. The latter chloride atoms lie very nearly in the plane of the benzene ring and the separations indicated as broken lines in Fig. 1 from the H(2) atoms are only 2.5 Å. This is half an Ångström less than the sum of the van der Waals' radii, and a strong interaction is therefore assumed to be present between these atoms.

The fact that the distances from the (»outer») N(2)-atom to the chloride ions are nearly equal to, and actually slightly shorter than the N(1)-Cl^{-} distances raises questions regarding the charge distribution within the diazonium ion. According to classical valence concepts the N(1)-atoms is considered equivalent to the nitrogen atom of an ammonium ion and is expected to carry the positive charge. However, the positive charge may not be expected to remain entirely unaffected on the N(1)-atom in the present ion as an electron transfer from other parts of the molecule, preferably from the outer nitrogen atom, seems

Table 5. Bond lengths and valence angles in the benzenediazonium ion. Numbers in parentheses are the corresponding estimated standard deviations.

N(1)-N(2)	:	1.097 Å	(0.006 Å)
N(1)-C(1)	:	1.385 Å	(0.009 Å)
C(1)-C(2)	:	1.374 Å	(0.008 Å)
C(2)-C(3)	:	1.383 Å	(0.010 Å)
C(3)-C(4)	:	1.376 Å	(0.008 Å)
N(2)-N(1)-C(1)	:	180°	
C(1)-C(2)-C(3)	:	117.6°	(0.7°)
C(2)-C(3)-C(4)	:	119.8°	(0.7°)
C(3)-C(4)-C(5)	:	121.7°	(0.7°)
C(6)-C(1)-C(2)	:	124.8°	(0.6°)

likely. The positive charge would then be shared between the nitrogen atoms; this might explain the approximate equidistance from a chloride ion to the two nitrogen atoms.

A further indication of an electron transfer from the outer to the inner nitrogen atom may be found in the results obtained for the thermal parameters of the nitrogen atoms according to the least squares refinement calculations in which the nitrogen atoms were both assigned the atomic form factor of a neutral nitrogen atom. Had the N(1) atom in fact been positively charged and the N(2) atom neutral, the refinement procedure would tend to place fewer electrons on the N(1) atom by increasing the B-value of the thermal effect expression by an amount of the order $1-2$ Å^{-2} relative to the B-value for the N(2)[6], provided that we ascribe nearly equal thermal vibrations to the nitrogen atoms. No such tendency was indicated (*cf.* Table 4).

The interatomic distances and valence angles in the benzenediazonium ion are listed in Table 5 together with their estimated standard deviations.

The N—N triple bond length was found equal to that observed in gaseous nitrogen. A small lengthening relative to this due to the formation of the adjacent N(1)—C(1) bond might have been expected; the opposing effect of the positive charge on the nitrogen atoms, however, has probably the same order of magnitude.

The N(1)—C(1) bond is 0.085 Å shorter than the aliphatic N—C bond; a corresponding bond shortening relative to the aliphatic C—C bond was found for the C(1)—C(7) bond in benzonitrile [7].

The N(2)—N(1)—C(1)————(C4) arrangement is for symmetry reasons strictly linear. Within the error of the measurements the benzenediazonium ion is planar, the distance from the C(2) and C(3) atoms to the »best fit» plane being less than 0.01 Å.

The carbon-carbon bonds are all found shorter than those in the benzene molecule (1.397 Å). The ratios of the difference between the benzene C—C bond length and the values found in the present compound to the estimated standard deviations are 2.9, 1.4 and 2.6 for the C(1)—C(2), C(2)—C(3) and C(3)—C(4) bonds, respectively. The corresponding probability values P are 0.2 %, 8 % and 0.5 %, and by the standards given by Cruickshank [5] the C(1)—C(2) and C(3)—C(4) bond lengths are significantly shorter than the benzene C—C bond, whereas the difference between the C(2)—C(3) bond length and the benzene value is not significant.

The distortion of the valence angles brought about by substitution of one of the hydrogen atoms by a N_2^+-group indicated by the very short $C(1)—C(4)$ distance found in the two-dimensional analysis [1] has been confirmed by the present investigation.

As may be seen from Table 5 the $C(6)—C(1)—C(2)$ and $C(3)—C(4)—C(5)$ angles are significantly larger than $120°$, in accordance with the shortness of the adjacent $C(1)—C(2)$ and the $C(3)—C(4)$ bonds, whereas the $C(1)—C(2)—C(3)$ angle is smaller than $120°$. The irregularities of the valence angles in the ring are analogous to what was found in a precision measurement of the structure of benzonitrile by microwave methods [7]. The inductive effect of the N_2^+ group must, however, be expected to be larger than that of the nitrile group and it is reasonable that the distortion is more pronounced in the present compound.

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