ACTA CHEMICA SCANDINAVICA 16 (1962) 1882–1889

The Crystal Structure of Benzenediazonium Tribromide

O. ANDRESEN and CHR. RØMMING

Universitetets Kjemiske Institutt, Blindern-Oslo, Norway

The crystal structure of benzenediazonium tribromide, $C_6H_5N_2Br_3$, has been determined by X-ray methods. The compound crystallizes in the monoclinic system with space group $C2/c$. The tribromide ions are situated in centers of symmetry and the benzenediazonium ions on two-fold axes. The Br—Br bond length is 2.543 Å; the N—N and N—C bond lengths in the diazonium ion are 1.11 and 1.41 Å, respectively.

Aryldiazonium trihalides were first prepared by Griess [1,2] who assumed their constitution to be analogous to that of tetraethylammonium periodide. Chattaway [3], on the other hand, preferred to formulate these compounds as Ar·NHal·$NHal_2$ since they may be prepared by letting halogen react directly with arylhydrazine. From the similarity between diazonium and alkali perhalides Hantzsch [4] and Forster [5] inferred, however, that the diazonium perhalides are true diazonium salts. Aroney and Le Fèvre [6] carried out an infrared spectroscopic investigation of several aryldiazonium tribromides, all of which gave a strong absorption band in the frequency range 2240—2250 cm^{-1}. An absorption band in this region is characteristic of the Ar·N_2^+-group, and they therefore concluded that the compounds consist of aryldiazonium and tribromide ions. The structure of neither of these types of ions has been determined with great accuracy, and it was decided to investigate the structure of crystalline benzenediazonium tribromide by X-ray methods.

EXPERIMENTAL

To a freshly prepared aqueous solution of benzenediazonium chloride was added the solution of bromine in a potassium bromide solution under continuous stirring and ice cooling. The brown oil formed was separated and allowed to loose bromine in a dry air stream at room temperature, and after a few days single crystals of benzenediazonium tribromide in the form of orange-yellow plates had been formed.

The compound decomposes at 63—64°C, but is stable in dry air at room temperature. Because of their sensitiveness towards moisture the crystals were kept in capillary tubes during the X-ray exposure. The intensity data were obtained from integrated Weissenberg films taken at −20°C using filtered CuK-radiation (λ = 1.542 Å), the crystals used in the X-ray work had cross sections of 0.1 × 0.1 mm^2. The intensities were measured

photometrically except for the weakest reflections, the intensities of which were estimated visually. The numbers of non-equivalent reflections observed were 56 in the ($hk0$)-zone, 92 in the ($0kl$)-zone and 39 in the ($h0l$)-zone, the maximum numbers obtainable with Cu$K\alpha$-radiation are 65, 101 and 46, respectively. Most of the calculations carried out during the structure determination were performed on a Ferranti "Mercury" computer, the two dimensional least squares refinement program was that set up by Curtis [7]. Atomic form factors given as an analytical approximation by Forsyth and Wells [8] were used in these calculations.

CRYSTAL DATA

Oscillation and Weissenberg photographs show that the crystals are monoclinic with the cell constants:

$a = 6.73$ Å, $b = 14.10$ Å, $c = 11.00$ Å, $\beta = 106.8°$.

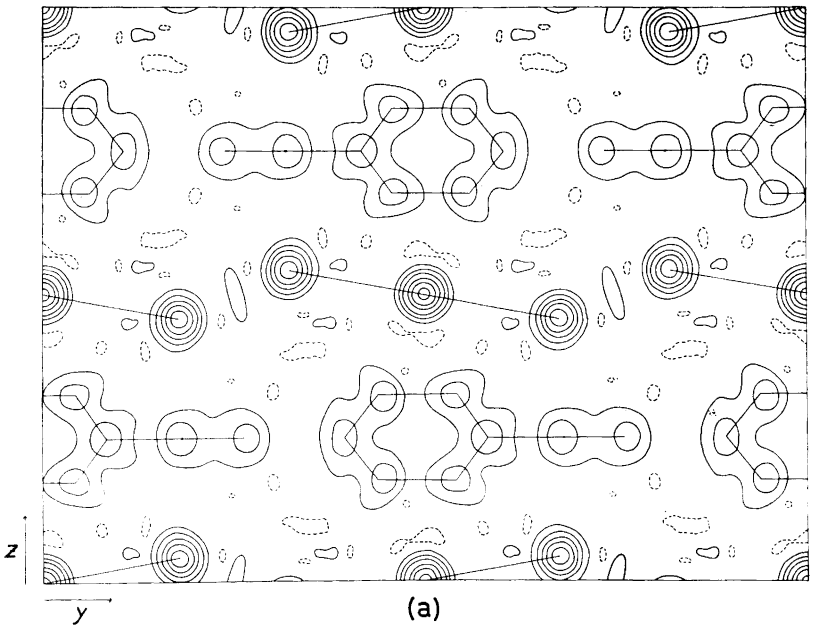
With *four* formula units per unit cell the calculated density is 2.31 g.cm^{-3}. Reflections are present only when $h + k = 2n$ and the condition for the presence of reflections in the ($h0l$)-zone is $l = 2n$. The space group is therefore either Cc or $C2/c$.

STRUCTURE DETERMINATION

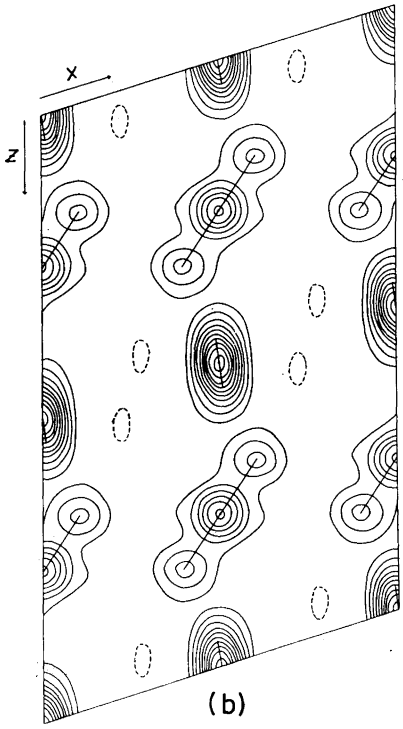
The space group Cc contains no centres of symmetry and requires one molecular unit in each of the four-fold general positions. The space group $C2/c$, on the other hand, is centrosymmetric with eight-fold general positions and requires symmetry elements to be present both in the diazonium and in the tribromide ions. As a working hypothesis the latter space group was first assumed to be the correct one, and in the course of the structure determination the correctness of this assumption was actually confirmed. The positions of the bromine atoms could be derived from Patterson projections along b and c. Fourier maps based on the observed structure factors and with signs calculated from these bromine parameters were worked out, and from these maps approximate positions of the light atoms could be deduced. Successive Fourier refinements in the three projections were carried out in the usual way until no further changes of signs occurred. The coordinates were then submitted to further refinements using the method of least squares, alternatingly treating the three data sets so that at any time the best values of the parameters for the unresolved atoms could be used. The R-values thus finally arrived at were $R_{0kl} = 8.0$ %, $R_{hk0} = 7.3$ %, $R_{h0l} = 7.3$ %. The tribromide group was found to be centrosymmetric, the central bromine atom coinciding

Table 1. Atomic coordinates, fractions of cell edges.

	x	y	z
Br_1	0	0	0
Br_2	0.0049	0.1775	0.0418
N_1	0	0.762	0.250
N_2	0	0.683	0.250
C_1	0	0.583	0.250
C_2	0.106	0.543	0.174
C_3	0.104	0.440	0.175
C_4	0	0.395	0.250



(a)



(b)

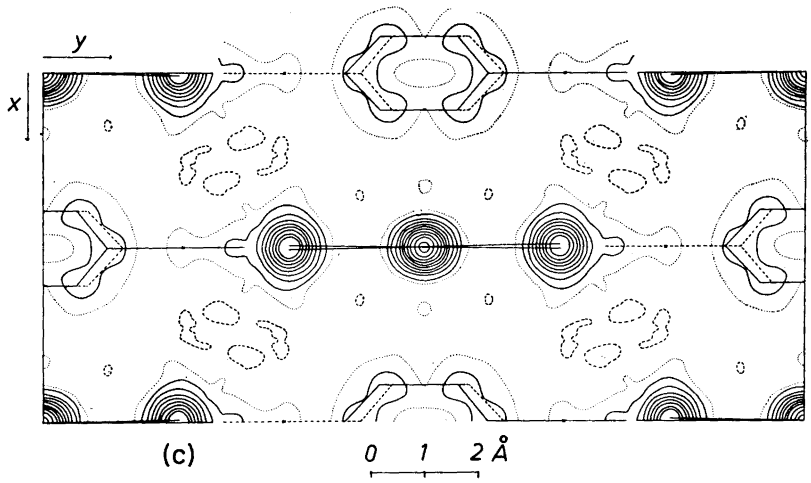


Fig. 1. Fourier projections of benzenediazonium tribromide, (a) along the *a* axis, (b) along the *b* axis and (c) along the *c* axis. Contour intervals 10 e Å^{-2} for bromine, 3 e Å^{-2} for carbon and nitrogen in (a) and 6 e Å^{-2} for carbon and nitrogen in (b) and (c).

with a centre of symmetry in the space group. The benzenediazonium ions are situated on two-fold axes running through the N_2—N_1—C_1---C_4 atoms.

The atomic parameters judged to be the most accurate are listed in Table 1. The *y* and *z* parameters were determined from the 0*kl*-data, the *x* parameter of C_2 and C_3 from the Fourier projection along *b* assuming a planar benzene ring, and for the *x* parameter of the "outer" bromine atom the mean value of those found from the *hk*0 and *h*0*l* data has been listed. Fourier maps of the three projections are reproduced in Fig. 1. A comparison of the observed and calculated structure factors is given in Table 2.

DISCUSSION OF THE STRUCTURE

It follows from the present structure determination that benzenediazonium tribromide crystals have ionic character and consist of centrosymmetric tribromide ions and benzenediazonium ions with symmetry C_2. Since the N_2, N_1 and C_1 atoms are situated on a two-fold symmetry axis and no anisotropic thermal effects were indicated it may be stated that the N—N—C arrangement of the diazonium ion is linear. In Table 3 some interatomic distances and valence angles in the benzenediazonium ion are listed, the indexing of the atoms being that used in Fig. 2. The standard deviations indicated are estimated using the formula given by Cruickshank [9]. The C—C bond distances (mean value 1.40 Å) are, within the accuracy of the structure determination, identical with those found in the benzene molecule. However, the symmetry of the carbon ring is not hexagonal; the C_6—C_1—C_2 and C_3—C_4—C_5 angles are significantly larger than the other angles in the ring and therefore,

Table 2. Observed and calculated structure factors for benzenediazonium tribromide.

h	k	l	F_o	F_c
0	0	2	204	206
		4	232	244
		6	74	68
		8	22	10
		10	24	− 36
		12	16	16
0	2	0	18	14
		1	56	− 58
		2	18	− 18
		3	112	−112
		4	16	10
		5	130	−134
		6	114	106
		7	78	− 82
		8	66	66
		9	46	− 50
		10	72	76
		11	6	− 8
		12	46	56
		13	< 4	6
0	4	0	66	68
		1	64	66
		2	56	56
		3	120	122
		4	64	58
		5	136	140
		6	86	76
		7	94	98
		8	58	54
		9	46	52
		10	52	52
		11	12	12
		12	30	34
		13	< 4	− 3
0	6	0	208	218
		1	36	− 32
0	6	2	240	244
		3	34	− 34
		4	128	126
		5	52	− 50
		6	64	60
		7	32	− 34
		8	10	4
		7	46	52
		10	6	− 8
		11	< 6	− 2
		12	< 5	− 13
0	8	0	82	− 74
		1	38	− 34
		2	22	− 14
		3	42	− 34
		4	18	14
		5	50	− 46
		6	42	38
		7	38	− 40
		8	72	74

h	k	l	F_o	F_c
		9	16	− 18
		10	54	66
		11	< 5	− 3
		12	24	42
0	10	0	66	62
		1	40	34
		2	76	70
		3	62	52
		4	70	66
		5	100	94
		6	28	24
		7	42	44
		8	40	38
		9	38	40
		10	12	16
		11	< 4	4
0	12	0	108	96
		1	30	− 24
		2	92	82
		3	38	− 32
		4	72	70
		5	44	− 42
		6	18	20
		7	36	− 36
		8	20	18
		9	16	− 18
		10	4	− 2
0	14	0	32	− 24
		1	6	− 2
		2	16	− 10
		3	6	− 4
		4	< 7	4
		5	< 7	− 4
		6	26	26
		7	4	− 4
		8	30	34
0	16	0	50	48
		1	6	6
		2	40	40
		3	32	26
		4	30	30
		5	20	20
		6	18	20
0	18	0	24	28
		1	< 3	− 5
2	0	2	148	140
4			124	112
6			64	72
$\bar{2}$			260	264
$\bar{4}$			184	176
$\bar{6}$			84	84
$\bar{8}$			28	32
2	0	4	212	196
4			112	108
6			40	44
$\bar{2}$			192	196

h	k	l	F_o	F_c
$\bar{4}$			160	156
$\bar{6}$			104	108
$\bar{8}$			44	56
2	0	6	36	28
4			< 7	15
6			< 4	11
$\bar{2}$			68	68
$\bar{4}$			40	36
$\bar{6}$			32	24
$\bar{8}$			24	24
2	0	8	20	16
4			20	24
$\bar{2}$			56	48
$\bar{6}$			68	56
$\bar{6}$			40	36
$\bar{8}$			9	12
2	0	10	< 7	1
4			< 3	3
$\bar{2}$			32	− 32
$\bar{4}$			16	− 20
$\bar{6}$			16	4
2	0	12	< 3	6
$\bar{2}$			24	16
$\bar{4}$			12	4
$\bar{6}$			< 4	2
1	1	0	140	132
	3		124	−115
	5		240	246
	7		105	100
	9		22	− 10
	11		103	102
	13		17	18
	15		< 7	1
	17		28	31
2	0	0	373	399
	2		26	− 26
	4		50	43
2	6	0	173	175
	8		41	− 42
	10		53	53
	12		71	70
	14		21	− 20
	16		23	27
3	1	0	138	137
	3		33	− 45
	5		148	159
	7		62	54
	9		23	− 24
	11		63	65
	13		8	10
	15		< 6	2
4	0	0	158	172
	2		18	− 33
	4		26	19
	6		106	113
	8		< 7	− 11

Table 2 continued.

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
10	42	46	11	32	33	7 1 0	31	28
12	48	52	13	5	5	3	< 6	− 8
14	< 6	− 12	6 0 0	74	79	5	30	36
5 1 0	81	80	2	< 7	− 12	7	17	14
3	< 7	− 15	4	18	10	9	< 3	− 4
5	77	83	6	49	54	8 0 0	23	36
7	35	26	8	< 7	− 5	2	8	1
9	6	− 18	10	19	24	4	7	5
			12	20	26			

assuming a planar molecule, certainly larger than 120°. The C_1-C_4 distance is somewhat shorter than in benzene, an effect also observed in benzenediazonium chloride [10]. The C—N and N—N bond lengths are in full agreement with the corresponding distances observed in the chloride.

The tribromide ion is centrosymmetric, the two equivalent Br—Br bond distances are 2.543 (estimated standard deviation 0.004 Å) in accordance with the results obtained by Romers and Keulemans [11], 2.53 and 2.54 Å in the tribromide ion in trimethylammonium bromide tribromide.

Yamasaki and Cornwell [12,13] have discussed the results of molecular quadrupole coupling measurements in dichloroiodides and concluded that the *p*-bonded model suggested by Pimentel [14] and Hach and Rundle [15] represents a better description for the bonding than the sp^3d_{zz} hybridization model earlier regarded to be the correct one for trihalide ions. They estimated the electronic charge distribution on the three atoms of the dichloroiodide ion and found that each of the symmetrically arranged chlorine atoms carries a negative charge, the central iodine atom being neutral or possibly carrying a formal positive charge. Havinga and Wiebenga [16] performed approximate calculations along the lines suggested by Pimentel on several polyhalides and were thus able to explain the structural features in some detail. They showed the negative trihalide ions to have the lowest energy in the linear configuration and that the charge distributions are in agreement with the results obtained by Yamasaki and Cornwell for the dichloroiodide ion: roughly one half electron charge on each of the outer halogens in a symmetrical configuration. The present investigation provides an experimental support for the view that the negative charge is situated on the outer halogen atoms insofar as every N_2^+ group has *outer* (Br_3^-) bromine atoms as its nearest neighbours (*cf.* Fig. 2),

Table 3. Interatomic distances and valence angles in the benzenediazonium ion. Figures in brackets are estimated standard deviations.

N_1-N_2 : 1.11 Å (0.05 Å)	$<C_1-C_2-C_3$: 114° (3°)
C_1-N_1 : 1.41 Å (0.05 Å)	$<C_2-C_3-C_4$: 118° (3°)
C_1-C_2 : 1.37 Å (0.04 Å)	$<C_2-C_1-C_6$: 131° (4°)
C_2-C_3 : 1.45 Å (0.05 Å)	$<C_3-C_4-C_5$: 125° (4°)
C_3-C_4 : 1.38 Å (0.04 Å)	
C_1-C_4 : 2.65 Å (0.05 Å)	

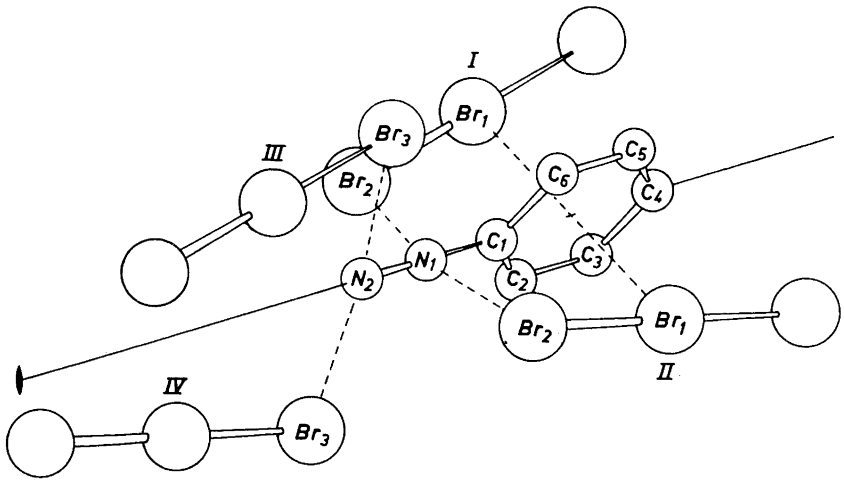


Fig. 2. Arrangement of tribromide ions about a benzenediazonium ion. The lines Br_1^I—Br_1^{II} and Br_3^{III}—Br_3^{IV} form angles of about 85° and 35° with the plane of the benzene ring, respectively.

while the central bromine atom is situated so close to the plane of a benzene ring that it is unlikely to carry a negative charge.

The spatial arrangement of tribromide ions about a diazonium ion is shown in Fig. 2. The tribromide ions I and III are related to II and IV by a two-fold axis of symmetry. The line Br_1^I—Br_1^{II} passes near the centre of the benzene ring and forms an angle of 85° with the ring plane. The bromine-benzene plane separation is 3.68 Å which is about 0.1 Å less than the sum of the van der Waals radius for bromine and the half-thickness of the benzene molecule. The shortest distance between a central bromine and a nitrogen atom is 4.34 Å.

The distances from the Br_2-atoms in the ions I and II to N_1 are 3.46 Å and from the Br_3-atoms in the ions III and IV to N_2 3.31 Å. It is remarkable that the shortest of the bromine to nitrogen distances is that to an outer nitrogen atom (N_2). According to classical valence concepts the N_1 atom is equivalent to an ammonium nitrogen atom and should therefore carry the positive charge. The short Br_3—N_2 distance would then indicate a van der Waals interaction and an electrostatic interaction exists only between the N_1 atom and the Br_2 atoms. However, the electron density of the triple bond may be displaced towards the N_1 atom (Sarkar [17]), in which case the positive charge is shared between the two nitrogen atoms. Electrostatic forces would then also be present between the Br_3 and N_2 atoms.

The Br_3—N_1 and the Br_2—N_2 distances are 3.76 and 3.65 Å, respectively.

REFERENCES

1. Griess, P. *Phil. Trans.* **157** (1864) 667; *Ann* **137** (1864) 50.
2. Griess, P. *J. Chem. Soc.* **20** (1867) 44.
3. Chattaway, F. D. *J. Chem. Soc.* **95** (1909) 862.
4. Hantzsch, A. *Ber.* **48** (1915) 1344.
5. Forster, M. O. *J. Chem. Soc.* **107** (1915) 260.
6. Aroney, M. and Le Fevre, R. J. W. *J. Chem. Soc.* **1955** 1630.
7. Curtis, A. R. *A.E.R.E. Mercury Autocode Program No. 29.*
8. Forsyth, J. B. and Wells, M. *Acta Cryst.* **12** (1959) 412.
9. Cruickshank, D. W. J. *Acta Cryst.* **2** (1949) 65.
10. Rømming, Chr. *Acta Chem. Scand.* **13** (1959) 1260.
11. Romers, C. and Keulemans, E. W. M. *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B.* **61** (1958) 345.
12. Yamasaki, R. S. and Cornwell, C. D. *J. Chem. Phys.* **30** (1959) 1265.
13. Cornwell, C. D. and Yamasaki, R. S. *J. Chem. Phys.* **27** (1957) 1060.
14. Pimentel, G. *J. Chem. Phys.* **19** (1951) 446.
15. Hach, R. J. and Rundle, R. E. *J. Am. Chem. Soc.* **73** (1951) 4321.
16. Havinga, E. E. and Wiebenga, E. H. *Rec. trav. chim.* **78** (1959) 724.
17. Sarkar, P. B. *J. Indian Chem. Soc.* **13** (1936) 19.

Received April 27, 1962.