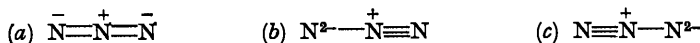## 164. *The Crystal Structure of Strontium Azide.*

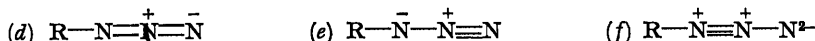### By F. J. LLEWELLYN and F. E. WHITMORE.

The structure of strontium azide has been completely determined by means of three-dimensional Fourier sections and lines using all the $\{hkl\}$ structure amplitudes obtainable with Cu-$K\alpha$ X-radiation. The structure is ionic, each strontium ion being surrounded by 8 azide ions, arranged in two sets, at distances 2·63 and 2·77 A., severally. The azide ion is linear and symmetrical, the nitrogen–nitrogen separation being 1·12 A.

THE azide grouping (N_3) has been shown by X-ray and electron-diffraction studies to be linear in both electrovalent and covalent substances. In the former, typified by sodium and ammonium azides (Frevel, *J. Amer. Chem. Soc.*, 1936, **58**, 779; *Z. Krist.*, 1936, **94**, *A*, 197) the two nitrogen–nitrogen separations in the azide ion are equal; the ion resonates between the three structures (*a*), (*b*), and (*c*),

$$(a) \ \overset{-}{N}\!=\!=\!\overset{+}{N}\!=\!=\!\overset{-}{N} \qquad (b) \ N^{2-}\!\!-\!\overset{+}{N}\!\equiv\!N \qquad (c) \ N\!\equiv\!\overset{+}{N}\!\!-\!N^{2-}$$

each of which is equally important, and stabilisation is effected by the considerable resonance energy; the nitrogen–nitrogen separation is 1·15 A. In the latter case, typified by cyanuric triazide (Knaggs, *Proc. Roy. Soc.*, 1935, **150**, *A*, 576), these two nitrogen–nitrogen bonds are not equivalent and the azide grouping has the dimensions shown in (I).

$$\underset{\substack{1\cdot26 \ \ 1\cdot11 \\ (I.)}}{R\!\!-\!\!N\!\!-\!\!N\!\!-\!\!N}$$

The three most probable resonance forms for the covalently linked azide group are (*d*), (*e*), and (*f*):

$$(d) \ R\!\!-\!\!N\!=\!\overset{+}{N}\!=\!\overset{-}{N} \qquad (e) \ R\!\!-\!\overset{-}{N}\!\!-\!\overset{+}{N}\!\equiv\!N \qquad (f) \ R\!\!-\!\overset{+}{N}\!\equiv\!\overset{+}{N}\!\!-\!N^{2-}$$

the last probably does not contribute to any appreciable extent, for it involves adjacent positive charges which render this form more unstable. Resonance therefore occurs between (*d*) and (*e*), leading to an unsymmetrical grouping of lower stability than the azide ion.

The stability of metallic azides to heat, friction, and impact varies considerably and is determined, at least in part, by the bonding between the metal and the azide group. Thus, the alkali-metal azides, which are ionic, are stable both to friction and to impact and are only decomposed gently by heat at 300—400°. The alkaline-earth azides are decomposed more violently by heat at a lower temperature (*ca.* 110—160°) but remain insensitive to friction and impact. On the other hand, azides of the heavier metals, *e.g.*, lead, and those of many of the B-sub-group elements, *e.g.*, copper and silver, decompose sometimes with explosive violence when lightly struck or rubbed.

Between these two extremes there is a large number of azides of intermediate properties in which it may be assumed that the linkage of the azide group is more or less covalent. The following investigation of the structure of strontium azide is the first of a series in which it is hoped to trace the development of covalent bonding with increasing instability.

Preliminary Crystallographic Data.—Small, well-defined, orthorhombic, bipyramidal (pseudo-tetragonal) crystals of strontium azide exhibiting the form {111} were obtained by slowly evaporating the aqueous solution to dryness in an Erlenmeyer flask. Single-crystal rotation photographs using Cu-$K\alpha$ X-radiation gave the cell dimensions: $[a] = 11\cdot82$, $[b] = 11\cdot47$, $[c] = 6\cdot08$ A. Oscillation photographs about the three principal axes revealed the halvings $\{hkl\}$ absent when $h + k \neq 2n$, $k + l \neq 2n$, $h + l \neq 2n$; $\{0kl\}$ absent when $k \neq 2n$, $l \neq 2n$, $k + l \neq 4n$; $\{h0l\}$ absent when $h \neq 2n$, $l \neq 2n$, $h + l \neq 4n$; and $\{hk0\}$ absent when $h \neq 2n$, $k \neq 2n$, $h + k \neq 4n$. The space-group is therefore F_{ddd}. The observed density is 2·73 g./c.c.; calculated for eight molecules in the unit cell, 2·77 g./c.c.

The space-group F_{ddd} accommodates 32 general positions, five sets of 16-fold special positions, and two sets of 8-fold special positions. Since there are 8 strontium ions in the unit cell, these must be located in one of the sets of 8-fold special positions, and because the choice between these is arbitrary, the co-ordinates may be written down as (000), (0½½), (½0½), (½½0), (¼¼¼), (¾¾¼), (¾¼¾), (¼¾¾).

The azide grouping can conveniently be dealt with in two parts: (*a*) the central nitrogen atoms, of which there are 16, must lie in one of the 16-fold special positions; and (*b*) the end nitrogen atoms, of which there are 32 located in the general positions, or in two sets of 16-fold positions.

(*a*) The five sets of 16-fold positions can be classified into two kinds; the first is centro-

3 M

symmetrical, and the second possesses two-fold axial symmetry. Thus, whatever the actual position of the azide group, it must possess either a centre of symmetry or a two-fold axis.

Measurement of Intensities.—The intensities of the diffracted beams from all the planes {*hkl*} observed by using Cu-$K\alpha$ X-radiation were obtained by visual estimation using a simple comparator on which a number of photographic spots produced by beams of known intensity had previously been recorded. From these intensities a set of structure amplitudes, on an arbitrary scale, can be obtained by using the relation $F = k\sqrt{ID p/L}$, the symbols of which are defined in an earlier paper (this vol., p. 838).

Usually it is convenient to render a set of relative structure amplitudes absolute by comparing directly a number of diffracted beams with some standard beam—normally the 400 reflection from the ground cleavage face of rock-salt. In this particular case we did not consider this to be necessary since the phases of nearly all the structure amplitudes could be deduced from the known position of the strontium atoms. When the structure was completed, the experimental structure amplitudes were made absolute by multiplying by the factor $F_{calc.}/F_{obs.}$. The table includes a list of the experimental structure amplitudes and also the calculated phases and structure amplitudes.

| *hkl.*	$F_{calc.}$	$F_{obs.}$	*hkl.*	$F_{calc.}$	$F_{obs.}$	*hkl.*	$F_{calc.}$	$F_{obs.}$
004	123	169	335	45	93	711	37	99
022	278	250	351	62	124	713	86	112
026	273	184	353	140	167	715	39	69
040	347	268	355	141	122	731	12	66
044	224	188	371	117	133	733	98	104
062	296	239	373	121	143	735	16	95
066	140	118	375	60	84	751	128	108
080	99	161	391	69	120	753	35	55
084	311	195	393	123	114	755	0	37
0, 10, 2	246	186	395	36	65	771	50	99
0, 12, 0	157	173	3, 11, 1	43	83	773	48	57
111	62	114	3, 11, 3	118	85	791	67	81
113	118	152	3, 13, 1	120	95	793	33	49
115	65	97	400	−71	<20	7, 11, 1	96	116
117	65	58	404	217	177	800	417	309
131	55	58	422	156	160	804	107	116
133	109	142	426	22	81	822	211	179
135	93	119	440	100	148	840	260	188
151	128	175	444	103	107	842	192	124
153	28	73	462	73	114	862	238	172
155	4	62	480	233	199	880	88	142
171	120	138	484	−22	56	8, 10, 2	216	144
173	83	79	4, 10, 2	48	98	911	16	91
175	25	81	4, 12, 0	115	88	913	97	95
191	79	118	511	193	168	915	34	73
193	46	76	513	76	113	931	10	67
195	47	73	515	110	115	933	76	82
1, 11, 1	92	118	531	199	191	935	56	85
1, 11, 3	70	63	533	107	110	951	72	102
1, 13, 1	10	46	535	69	83	953	19	48
202	233	208	551	89	98	971	63	95
206	155	144	553	142	140	973	−21	134
220	285	250	555	127	111	991	70	86
222	124	100	571	99	112	10, 0, 2	172	151
224	132	184	573	143	123	10, 2, 0	247	152
242	211	188	575	78	64	10, 2, 4	130	113
246	143	127	591	73	106	10, 4, 2	180	115
260	195	191	593	143	94	10, 6, 0	142	148
262	130	59	5, 11, 1	87	80	10, 8, 2	133	123
264	168	150	602	183	184	11, 1, 1	73	114
282	174	173	606	89	138	11, 1, 3	72	73
2, 10, 0	144	165	620	134	248	11, 3, 1	134	113
2, 10, 4	148	109	622	−101	60	11, 3, 3	53	64
2, 12, 2	140	110	624	161	146	11, 5, 1	127	71
311	164	228	642	156	150	11, 7, 1	94	97
313	86	124	646	113	127	12, 0, 0	−14	44
315	114	219	660	176	177	12, 2, 2	66	107
317	115	120	682	118	150	12, 4, 0	87	97
331	214	232	6, 10, 0	153	152	13, 1, 1	132	96
333	76	121	6, 10, 2	153	152	13, 3, 1	120	94

Determination of the Structure.—The strontium atoms located at (000), etc., will be in phase and contribute to all the observed (*hk*0), (*h0l*), and 0*kl* planes. Since the contributions of the

strontium atoms will in general be greater than that of the nitrogens, as a first approximation, the phase of these planes was taken as 0°, or, in other words, these structure amplitudes are positive. A Fourier projection on the c-plane using all the $hk0$ structure amplitudes was therefore computed in order to determine the approximate co-ordinates of the atoms of the azide group. Two peaks were observed having (xy) co-ordinates $(0\cdot125, 0\cdot000)$ and $(0\cdot125, 0\cdot075)$. It therefore appeared likely that the central nitrogen atom was located on the two-fold axis which passes through the origin and is parallel to the $[a]$ axis. That the atoms of the azide group have x co-ordinates approximately equal to $0\cdot125$ is indicated by the relative magnitudes of F_{400} — very small, F_{800} — very large, F_{1200} — very small; F_{h00} being calculable by the equation

$$F_{h00} = 8f_{Sr} + 16f_{N \text{ centre}} \cos 2\pi hx + 32f_N \cos 2\pi hx$$

Having thus established that the central nitrogen atom lies along the $[a]$ axis, two possibilities arise : the peak observed at (xy) co-ordinates $(0\cdot125, 0\cdot000)$ may be due to an atom having (xyz) co-ordinates $(0\cdot125, 0\cdot000, 0\cdot000)$ leading to the 16 positions $(0\cdot125, 0\cdot000, 0\cdot000)$, $(- 0\cdot125, 0\cdot000, 0\cdot000)$, $(0\cdot375, 0\cdot250, 0\cdot250)$, $(0\cdot125, 0\cdot250, 0\cdot250)$, $(0\cdot125, 0\cdot500, 0\cdot500)$, $(- 0\cdot125, 0\cdot500, 0\cdot500)$, $(0\cdot375, 0\cdot750, 0\cdot750)$, $(0\cdot125, 0\cdot750, 0\cdot750)$, $(0\cdot625, 0\cdot000, 0\cdot500)$, $(0\cdot375, 0\cdot000, 0\cdot500)$, $(0\cdot875, 0\cdot250, 0\cdot750)$, $(0\cdot625, 0\cdot250, 0\cdot750)$, $(0\cdot625, 0\cdot500, 0\cdot000)$, $(0\cdot375, 0\cdot500, 0\cdot000)$, $(0\cdot875, 0\cdot750, 0\cdot250)$, $(0\cdot625, 0\cdot750, 0\cdot250)$, or to an atom at $(0\cdot375, 0\cdot000, 0\cdot000)$ leading to 16 positions as above. It will be readily seen that these two possibilities reduce to the same set of (xy) co-ordinates.

FIG. 1.
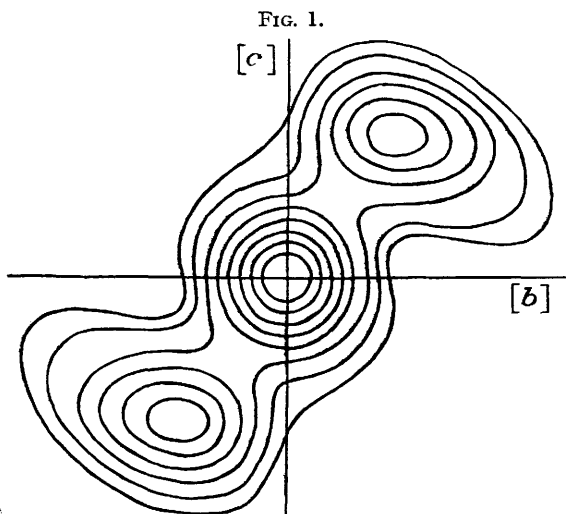
The atomic co-ordinates $(0\cdot125, 0\cdot000, 0\cdot000)$ for the central nitrogen are extremely improbable since the separation from the strontium atom at the origin would then be only $1\cdot47$ A., considerably less than the sum of the Sr^{2+} and N^- radii. Attention was therefore directed to the other possibility in which the two nitrogen atoms have the approximate co-ordinates

$$N_1 \text{ centre } 0\cdot375 \quad 0 \quad 0 \qquad N_2 \quad 0\cdot375 \; y \; z$$

The three-dimensional Fourier line, parallel to the $[a]$ axis, passing through the point $x = 0$, $y = 0$ showed a large maximum at $x = 0\cdot375$. A three-dimensional Fourier section parallel to the a-plane at a height $x = 0\cdot375$ led to (yz) co-ordinates $(0\cdot075, 0\cdot083)$ for the terminal nitrogen atom of the azide group. Further, three-dimensional Fourier lines and sections were then computed in order to refine these co-ordinates; during this process only a small number of those structure amplitudes towards which the strontium atoms contribute changed sign, but there was a general rearrangement in those for which the strontium contribution is zero. The final co-ordinates, derived from the Fourier section shown in Fig. 1 and the three-dimensional Fourier lines parallel to the $[a]$ axis, are :

$$Sr \quad 0 \quad 0 \quad 0 \qquad N_1 \quad 0\cdot383 \quad 0 \quad 0 \qquad N_2 \quad 0\cdot383 \quad 0\cdot058 \quad 0\cdot148$$

The agreement between the observed and the calculated structure amplitudes (the average descrepancy is 27%) is not of the same order as it is now customary to expect in structural determinations of organic substances; this may be attributed to the presence of the very heavy

strontium atom, which renders intensity measurements difficult; the contribution of the azide ion to the observed intensity is probably of the order of the experimental error for a high proportion of the planes.

Discussion of the Structure.—The equivalence of the two nitrogens at either end of the azide group—each is separated from the central nitrogen by 1·12 A.—shows that the structure is ionic. Fig. 2 represents the disposition of the nearest azide ions around any strontium ion. The

FIG. 2.
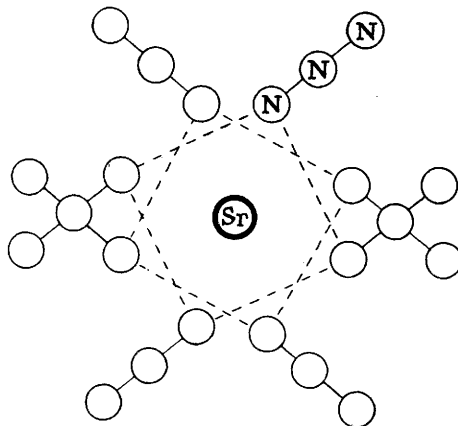
strontium ion has eight near neighbours; these can conveniently be classified in two sets of four. In the first set the strontium–nitrogen separation is 2·63 A., and in the second set 2·77 A. Each azide ion is disposed between four strontium ions, two at a distance of 2·77 A. and two at 2·63 A.

Experimental. Strontium carbonate (5 g.) was dissolved in 2% hydrazoic acid (30 ml.) and the solution concentrated on a water-bath; on cooling, a mass of extremely small crystals was deposited. Larger crystals suitable for X-ray photography were obtained from the mother-liquor by slow evaporation in an Erlenmeyer flask.