

# THE CRYSTAL STRUCTURE OF TETRAMETHYLAMMONIUM IODIDE

BY

WILLIAM ZACHARIASEN

WITH ONE FIGURE IN THE TEXT

In the present note are given briefly the results of an X-ray investigation on tetramethylammonium iodide,  $N(CH_3)_4J$ . The examination was carried out in the Mineralogical Institute of the University Oslo at the proposal of professor Dr. V. M. GOLDSGHMIDT. Both rotation photographs and powder photographs were used.

The structure of  $N(CH_3)_4J$  has been examined by L. VEGARD<sup>1</sup>, L. VEGARD and T. HAUGE<sup>2</sup> and by G. GREENWOOD<sup>3</sup>. While GREENWOODS paper only deals with the space group, VEGARD in his two papers has used the observed intensities also for determination of the atomic arrangement. Although the structure proposed by VEGARD and HAUGE gives satisfying agreement with the observed intensities, it conflicts with crystallochemical facts. The present investigation was therefore undertaken in order to find an atomic arrangement agreeing both with the observed intensities and with the crystallo-chemistry.

GREENWOOD based his deduction of the space group on rotation photographs. My figures show, however, that he has not succeeded in giving the reflexions their correct indices, apparently due to a small dissolving power of his camera. For example describes he the reflections 212, 412 and 612 as 202, 402 and 602. His results with regard to the space group are thus not reliable. He finds that the space group cannot be holohedral; but etching figures which I have prepared don't show any deviation from holohedral symmetry. As etching figures never posses higher symmetry than the crystal itself, we must assume that  $N(CH_3)_4J$  crystallizes in the ditetragonal-bipyramidal symmetry class<sup>4</sup>.

---

<sup>1</sup> Phil. mag. 33, 395, 1917.

<sup>2</sup> Skr. Norske Videnskapsakademi Oslo Nr. 10. 1926.

<sup>3</sup> Min. Mag. 21, 258, 1927.

<sup>4</sup> Lauephotographs which I have prepared also show holohedral symmetry.

My rotation photographs confirmed the unit cell containing two molecules found by VEGARD already in 1917.<sup>1</sup> Some of the observed data are compiled in the following tables.

### Rotation Photograph around (001).<sup>2</sup>

Table 1. *Determination of the c-axis.*

n	2 e	$\frac{2e}{2r}$	c
1	32,5	0,357	5,74 Å
2	82,0	0,900	5,78 Å

} 5,76 Å

Table 2. *Reflexions (h k 0).*

2 d	Intensity obs.	$V_2$ K = 0,4°	$\sin^2 \frac{V}{2} = \frac{\lambda^2}{4a^2} = (h^2 + k^2)$	h k 0
42,0	s	12,8	0,049	β 200
46,0	st	14,1	0,059 = 4 × 0,0148	200
66,0	ss	20,4	0,122	β 310
73,0	s-st	22,6	0,148 = 10 × 0,0148	310
84,0	ss	26,05	0,193	β 400
93,0	s-st	28,85	0,233 = 16 × 0,0146	400
100,0	sss	31,1	0,267 = 18 × 0,0148	330
105,0	s	32,65	0,291 = 20 × 0,0146	420
109,5	sss	34,0	0,313	β 510
122,5	s-st	38,15	0,382 = 26 × 0,0147	510
144,0	s +	44,95	0,499 = 34 × 0,0147	530
149,0	s-st	46,50	0,526 = 36 × 0,0146	600
160,0	s-st	49,95	0,586 = 40 × 0,0147	620
188,5	s-st	58,95	0,734 = 50 × 0,0147	550, 710
194,5	s-st	60,85	0,763 = 52 × 0,0147	640
207,5	ss	64,90	0,820	β 820
215,5	s-st	67,45	0,853 = 58 × 0,0147	730

Mean value of  $\frac{\lambda^2}{4a^2} = 0,01466$  ∴ a = 7,99 Å

<sup>1</sup> loc. cit.

<sup>2</sup> For the rotation photographs was a camera of diameter 91 mm. used. All diagrams are taken with iron radiation. st strong, s = weak in the tables.

Table 3. *Reflexions (h k 1).*

2 d	Intensity obs.	$\frac{\vartheta}{2}$ K = 0,3°	$\sin^2 \frac{\vartheta}{2}$ obs.	h k 1	$\sin^2 \frac{\vartheta}{2}$ calc.
33,5	st	13,8	0,057	111	0,058
47,0	st	17,15	0,087	201	0,087
52,5	s st	18,6	0,102	211	0,102
67,5	ss	22,7	0,149	221	0,146
71,0	s	23,7	0,161	301	0,160
75,0	st	24,75	0,175	311	0,175
86,0	sss	27,9	0,219	321	0,219
89,5	sss	28,9	0,234	β 411	0,229
96,5	s +	30,95	0,264	401	0,263
99,5	st	31,85	9,278	411	0,278
109,0	s-st	34,6	0,322	421	0,322
112,5	ss	35,7	0,340	β 511	0,337
123,5	s	38,95	0,395	501, 431	0,395
126,5	st	39,8	0,410	511	0,410
135,0	s	42,3	0,453	521	0,454
149,0	s+	46,5	0,526	531	0,527
154,0	ss	48,0	0,552	601	0,556
157,5	s	49,0	0,570	611	0,571
166,5	s	51,75	0,617	621	0,615
169,5	s	52,6	0,631	541	0,629
181,5	ss	56,1	0,690	631	0,688
194,5	ss +	59,95	0,749	701	0,747
198,0	st	60,95	0,764	711, 551	0,761
205,0	s	62,95	0,793	641	0,791
208,5	s-st	63,95	0,807	721	0,805
230,0	st	69,85	0,881	731	0,879

Table 4. *Reflexions (h k 2).*

2 d	Intensity obs.	$\frac{\vartheta}{2}$ K = 0,2°	$\sin^2 \frac{\vartheta}{2}$ obs.	h k 2	$\sin^2 \frac{\vartheta}{2}$ calc.
53,5	st	25,7	0,188	212	0,188
76,0	s-st	29,85	0,248	302	0,245
94,0	st	33,6	0,306	322	0,304
110,0	st	37,2	0,365	412	0,363
139,5	st	44,0	0,483	502, 432	0,480
154,0	st	47,4	0,542	522	0,539
184,0	st	54,25	0,659	612	0,656
200,0	st	57,75	0,715	542	0,715
219,0	st	61,5	0,772	632	0,773

Table 5. *Rotation Photograph around (100).*

n	2 e	$\frac{2 e}{2 r}$	a
1	22,5	0,247	8,06
2	50,0	0,549	8,03
3	96,0	1,055	7,99

} 8,03 Å

Table 6. *Powder Photograph.*

2 d	$\frac{\theta}{2}$ K = 0,50	$\sin^2 \frac{\theta}{2}$ obs.	h k l	$\sin^2 \frac{\theta}{2}$ calc.	Int. obs.
25,95	11,90	0,0425	101	0,0433	1
27,4	12,62	0,0477	$\beta$ 111 200	0,0483	1
30,05	13,95	0,0581	111 200	0,0581 0,0593	10
35,9	16,86	0,0841	$\beta$ 211	0,0844	0,5
36,5	17,16	0,0871	201	0,0878	0,5
39,5	18,66	0,1024	211	0,1026	3
42,55	20,19	0,1191	220	0,1186	1
44,2	21,00	0,1285	102	0,1288	3
47,4	22,60	0,1477	221	0,1471	4
48,4	23,10	0,1539	310	0,1482	1
51,9	24,84	0,1765	$\beta$ 212	0,1547	1,4
53,5	25,64	0,1872	311	0,1767	3
58,4	28,09	0,2217	212	0,1881	3
60,5	29,14	0,2371	321	0,2212	1,5
61,9	29,83	0,2475	400	0,2371	1
64,3	31,03	0,2657	302	0,2474	2,5
64,9	31,33	0,2704	401	0,2656	1,5
66,2	31,98	0,2805	330	0,2668	1,5
68,2	32,98	0,2963	103	0,2712	1,5
69,5	33,63	0,3068	411	0,2804	1,75
71,75	34,75	0,3249	331	0,2953	1,75
72,4	35,07	0,3301	420	0,2964	1
76,8	37,27	0,3667	322	0,3067	2,5
77,9	37,82	0,3760	421	0,3249	1
79,5	38,61	0,3895	213	0,3305	1,5
80,5	39,11	0,3980	412	0,3659	1,25
82,5	40,11	0,4151	223	0,3750	0,5
86,3	42,01	0,4479	510	0,3853	1
87,4	42,56	0,4575	303	0,3898	1
90,5	44,10	0,4843	501	0,3990	1,25
93,0	45,35	0,5061	431	0,4138	1,75
93,9	45,80	0,5139	511	0,4138	1,75
96,0	46,85	0,5323	323	0,4491	1,5
97,4	47,54	0,5443	521	0,4583	0,5
98,3	47,99	0,5520	114	0,4854	5
103,25	50,37	0,5932	432, 502	0,4845	5
104,2	50,94	0,6030	530, 413 441	0,5039 0,5083 0,5027	4
106,8	52,23	0,6248	204	0,5151	2
			600, 531 214	0,5335 0,5324 0,5299	3
			522	0,5438	3
			423	0,5528	1
			620	0,5928	3
			314	0,6040	4
			503	0,6269	4
			433		4

$$\sin^2 \frac{\theta}{2} = 0,01482 (h^2 + k^2) + 0,02849 l^2$$

$$a = 7,94 \text{ \AA} \quad c = 5,73 \text{ \AA}$$

Fe-radiation      Camera diameter 57,45 mm.

Table 7.

Compound	$\frac{c}{a}$	a	c	Space Group	Coordinates of	
					Iodine	Nitrogen (Phosphorus)
NH <sub>4</sub> J <sup>1</sup>	0,707	6,18	4,37	...	(0 $\frac{1}{2}$ 0,50) ( $\frac{1}{2}$ 0 0,50)	(000) ( $\frac{1}{2}$ $\frac{1}{2}$ 0)
PH <sub>4</sub> J	0,729	6,34	4,62	D <sub>4</sub> h <sup>7</sup>	(0 $\frac{1}{2}$ 0,40) ( $\frac{1}{2}$ 0 0,60)	(000) ( $\frac{1}{2}$ $\frac{1}{2}$ 0)
N(CH <sub>3</sub> ) <sub>4</sub> J	0,724	7,94	5,75	D <sub>4</sub> h <sup>7</sup>	(0 $\frac{1}{2}$ 0,39) ( $\frac{1}{2}$ 0 0,61)	?
P(CH <sub>3</sub> ) <sub>4</sub> J <sup>2</sup>	0,731	6,04	(8,26)	...	---	---

Table 8. *Calculated Intensities.*

h k l	Intensities				h k l	Intensities			
	Zach.		Vegard			Zach.		Vegard	
	calc.	obs.	obs.	calc.		calc.	obs.	obs.	calc.
001	} 0,5		1,5	2,5	331	} 2,4	1,75	1	0,9
110					420				
101	} 0,7	1	1,5	2,2	322	} 3,8	2,5	2,5	2,4
111									
200	} 4,0	10	10	10	213	} 2,4	1,5	} 3	3,1
201					0,9				
211	} 2,2	3	5	3	223	} 0,7	0,5	0	0,3
220					1,2				
102	} 1,9	3	3	2,2	303	} 4,1	1,25	1,2	0,8
221					2,5				
310	} 3,0	3	3	1,3	431	} 3,0	1,75	1,2	0,6
311					3,0				
212	} 3,8	3	3	1,9	323	} 2,4	1,5	1	0,8
321					1,2				
400	} 1,2	1	0,5	0,8	114	} 6,4	5	3	1,9
302					1,9				
401	} 2,3	1,5	} 2,5	2,1	502	} 7,9	4	2,5	3,9
330					2,3				
103	} 1,4	1,5	} 1,5	2,1	441	} 7,9	4	2,5	3,9
411					3,1				

The best figures for the dimensions are:

$$a \quad 7,941 \pm 0,006 \text{ \AA}, \quad c = 5,749 \pm 0,006 \text{ \AA}$$

$$c/a \quad 0,7240$$

Calculated density 1,835.

GROTH<sup>4</sup> gives  $c/a = 0,7223$  (SLAVIK) and the density 1,827 1,844.

<sup>1</sup> The CsCl-modification treated as tetragonal with two molecules in the tetragonal cell.

<sup>2</sup> The lattice dimensions are calculated from the density 1,749, L. WAGNER Zeitschr. f. Krist. 50, 47, 1912.

<sup>3</sup> Coincidence with  $\frac{2}{3}$  311.

<sup>4</sup> Chemische Krystallographie I, p. 193.

As odd values of  $h^2 + k^2 + l^2$  are observed, the structure has to be based on a simple tetragonal lattice.

In a compound like  $N(CH_3)_4J$ , where both heavy and light atoms are present, the influence of the glancing angle on the scattering power is of the greatest importance. If we neglect the F-curves we probably will obtain quite wrong results. Absolute intensity measurements have shown that the F-curves calculated by HARTREE'S<sup>1</sup> data are sufficiently accurate in the most cases. In the present case, however, HARTREE'S figures cannot be used for a calculation of the scattering power of N and C, as we do not know anything about the nature of the binding inside the group  $N(CH_3)_4^+$ . Whatever assumptions we make with regard to the state of ionization, it is, however, obvious that for relative large glancing angles the reflecting power of iodine is many times that of nitrogen and carbon. We can therefore as a first (and really very close) approximation consider the reflections to be due to the iodine atoms alone.

The rotation photographs show that a lot of reflexions are absent, namely  $h k 0$  when  $h + k$  is odd and  $h k 2$  when  $h + k$  is even. As the unit cell contains only two iodine atoms, we have to place them in positions  $(0 \frac{1}{2} u)$   $(\frac{1}{2} 0 \bar{u})$  with  $u = ca \frac{3}{8}$ , to obtain the above regularities. Using the following reflections occurring at large glancing angles, 522, 423, 620, 314, 503, 433, we find  $u = 0,390 \pm 0,015$ . The positions  $(0 \frac{1}{2} u)$   $(\frac{1}{2} 0 \bar{u})$  for iodine are possible only in the space group  $D_{4h}^7$ , which is the same as found by VEGARD.

The space group  $D_{4h}^7$  allows the N atoms to possess coordinates  $(0 \frac{1}{2} v)$   $(\frac{1}{2} 0 \bar{v})$ ,  $(0 0 0)$   $(\frac{1}{2} \frac{1}{2} 0)$  or  $(0 0 \frac{1}{2})$   $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ . Due to the small reflecting power of nitrogen a distinction between these three possibilities cannot be made by intensity observations. According to the crystallochemistry the structure of  $N(CH_3)_4J$  must be closely related to the analogous compounds:  $NH_4J$ ,  $PH_4J$  and  $P(CH_3)_4J$ . The following table prove that this relation really exists and force us to choose the coordinates  $(0 0 0)$   $(\frac{1}{2} \frac{1}{2} 0)$  for the nitrogen atoms.

Further applying the principle of analogy, we must assume that 4  $CH_3$ -groups tetrahedrally surround each N-atom. The 8 C-atoms then have the positions:

$$\begin{aligned} &(u 0 v) (0 u \bar{v}) (u + \frac{1}{2} \frac{1}{2} \bar{v}) (\frac{1}{2} u + \frac{1}{2} v) \\ &(\bar{u} 0 v) (0 \bar{u} \bar{v}) (\frac{1}{2} - u \frac{1}{2} \bar{v}) (\frac{1}{2} \frac{1}{2} - u v) \end{aligned}$$

The tetrahedrons are regular when  $u = v$ .

<sup>1</sup> Phil. mag. 50, 289, 1925.

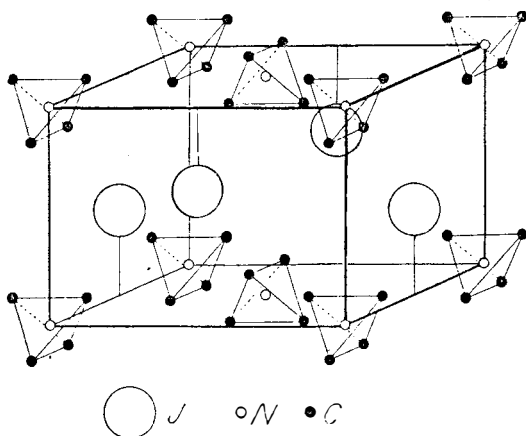


Fig. 1.

The accuracy with which we can fix the positions of the C-atoms is, however, very small, due in the first place to their small reflecting power and in the second place to the fact that we do not know the F-curves. Assuming the scattering power of iodine, carbon and nitrogen to be roughly proportional to 10, 1 and 1,<sup>1</sup> we find that  $u$  and  $v$  lie between  $\frac{1}{2}$  and  $\frac{1}{6}$ .

In table 8 are the intensities calculated according to the usual formulae for imperfect crystals:

$$I \sim \frac{F^2}{\sin^2 \frac{\theta}{2}} s \frac{1 + \cos^2 \theta}{\cos \frac{\theta}{2}}$$

For carbon the parameters  $u = v = \frac{1}{8}$  were used. The agreement is satisfying. In Fig. 1 is the atomic arrangement reproduced. The distances are:

$$\begin{array}{l} \text{N J} \quad 4,54 \text{ \AA} \text{ and } 5,25 \text{ \AA} \\ \text{C C} \quad \text{ca } 2,0 \text{ \AA} \text{ and } \text{C N} \quad \text{ca } 1,2 \text{ \AA} \end{array}$$

Referring the positions of VEGARD and HAUGES structure to the origin used in the present paper, we obtain the following figures:

$$\begin{array}{l} \text{J } (0 \frac{1}{2} u) \quad (\frac{1}{2} 0 \bar{u}) \quad u = 0,389 \\ \text{N } (0 \frac{1}{2} v) \quad (\frac{1}{2} 0 \bar{v}) \quad v = 0,013 \\ \text{C } (u 0 v) \quad (0 u \bar{v}) \quad (u + \frac{1}{2} \frac{1}{2} \bar{v}) \quad (\frac{1}{2} u + \frac{1}{2} v) \\ (\bar{u} 0 v) \quad (0 \bar{u} \bar{v}) \quad (\frac{1}{2} -u \frac{1}{2} \bar{v}) \quad (\frac{1}{2} \frac{1}{2} -u v) \quad u = 0,111 \quad v = 0,083 \end{array}$$

<sup>1</sup> In the lack of exact knowledge.

The arrangement of the iodine and carbon atoms is thus within the error identical with mine. The nitrogen atoms, however, have in VEGARD and HAUGES structure a highly different arrangement, and the structure loses thereby fully its plausibility from a chemical point of view. According to the structure proposed by VEGARD and HAUGE we must write the formula  $(\text{CH}_3)_4(\text{NJ})$ . Chemical facts, however, prove the existence of a group  $\text{N}(\text{CH}_3)_4^+$ .

VEGARD tried to treat his atomic arrangement as a packing of spheres N, C, H and J. His attempt failed however as he had to give the iodine atoms the shape of a rotational body, like an egg. My structure gives no reason for the assumption that the iodine atoms are not spherical. On the other hand it seems to me to be quite unjustifiable to look at the structure of a compound like  $\text{N}(\text{CH}_3)_4\text{J}$  as a packing of spheres. That way of looking at a structure is most usefull by coordination lattices of atoms or atom ions; but cannot with success be extended to radicals and compounds where the nature of the binding is homoeopolar, and where the atoms consequently have no spherical symmetry. In the present case it seems justifiable to regard the binding between  $\text{N}(\text{CH}_3)_4^+$  and J as heteropolar; but the constituents of the group  $\text{N}(\text{CH}_3)_4^+$  are surely held together by forces of homoeopolar origin. No reason is thus present for the existence of the H-atoms as spherical units of the structure; it is far more plausible that they with the C-atoms form radicals  $\text{CH}_3$ , in which they have lost their geometrical individuality<sup>1</sup>.

A comparison of the atomic distances in the related compounds  $\text{NH}_4\text{J}$ ,  $\text{PH}_4\text{J}$ ,  $\text{N}(\text{CH}_3)_4\text{J}$  and  $\text{P}(\text{CH}_3)_4\text{J}$  is given in the following table.

$\text{NH}_4$	J	3,79 Å (at $\div 15^\circ \text{C}$ )
$\text{PH}_4$	J	3,67 Å and 4,21 Å <sup>2</sup>
$\text{N}(\text{CH}_3)_4$	J	4,54 Å and 5,25 Å
$\text{P}(\text{CH}_3)_4$	J	= 4,78 Å and 5,50 Å

$\text{NH}_4\text{J}$  is not quite isomorphous with the three other compounds, and this is obviously due the fact that  $\text{NH}_4^+$  has spherical symmetry, while the internal structure of the radicales  $\text{PH}_4^+$ ,  $\text{N}(\text{CH}_3)_4^+$  and  $\text{P}(\text{CH}_3)_4^+$  appears in a deviation from spherical symmetry.

<sup>1</sup> As the H-atoms in  $\text{NH}_4$

<sup>2</sup> The structure of  $\text{PH}_4\text{J}$  is found by R. G. DICKINSON, Journ. Amer. Chem. Soc. 44, 1489, 1922.



It is of interest to notice that P. NIGGLI<sup>1</sup> in a reference of VEGARDS paper of 1917 proposed, as a more plausible structure than VEGARDS, an atomic arrangement which is very similar to that found in the present paper. He assumed that the arrangement of the iodine and carbon atoms in VEGARDS structure was nearly correct, but moved the nitrogen atoms into the middle of the tetragonal bisphenoids formed by the carbon atoms.

In his second paper VEGARD, however, had to turn these bisphenoids  $90^\circ$  around the c-axis in order to get agreement with the observed intensities. As already mentioned is this arrangement of the Carbon atoms within the error identical with that found by me. The structure proposed by NIGGLI is thus not correct, although it is plausible from a chemical point of view and do not lead to improbable atomic distances.

---

<sup>1</sup> Zeitschr. f. Krist. 56, 213. 1921.

Oslo, Mineralogical Institute of the University,  
October 24th, 1927.

