That such is practically the case was shown by the fact that the gas evolved consisted of $Si Fl_4$ and that the substance left behind in the boat was found to be almost pure sodium chloride.

A better method of preparing amorphous silicon seemed to be the decomposition of silicon chloride by sodium. When boiled in benzene-solution with sodium or potassium no action took place. A reaction, however, took place on heating sodium in the vapour of silicon chloride, but it became very violent; the brown powder obtained could certainly be readily freed from sodium chloride by means of water, but on heating in a current of chlorine a large amount of $Si O_2$ (about 30%) was left behind showing that even this process does not lead to pure amorphous silicon.

Much more simple is the preparation of *crystallised* silicon according to the method recently published by R. A. Kühne (Chem. Centr. 1904, I. 64) if we introduce a slight modification. A mixture of 200 grams of aluminium shavings or powder, 250 grams of sulphur and 180 grams of fine sand is put into a Hessian crucible placed in a bucket with sand. Upon the mixture is sprinkled a thin layer of magnesium powder and this is ignited by means of a Goldschmidt cartridge. The mass burns with a beautiful light and the contents of the crucible become white hot. When cold, the mass is treated with dilute hydrochloric acid, which dissolves the aluminium sulphide and leaves the silicon in a beautifully crystallised state. The yield amounts to about 30 grams. On heating in a current of chlorine $Si Cl_4$ is very readily formed, only 3% remaining as non-volatile products. It is a material eminently suited for the preparation of $Si Cl_4$, but Mr. Slijper did not succeed in converting it into silicon sulphide by heating with sulphur.

Groningen, Lab. Univers. March 1904.

Crystallography. — *"On the preservation of the crystallographical symmetry in the substitution of position isomeric derivatives of the benzene series"*. By Dr. F. M. Jaeger. (Communicated by Prof. A. P. N. Franchimont).

(Communicated in the meeting of June 24, 1904).

Some time ago when engaged in a research as to the connection between molecular and crystallographical symmetry of position-isomeric benzene derivatives[1]), I demonstrated, that of the six possible *tribromo-*

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1) Jaeger, Crystallographic and Molecular Symmetry of position-isomeric Benzene-derivatives. Dissertation, Leiden 1903. (Dutch).

toluenes, the 1-2-4-6 and the 1-2-3-5 derivatives exhibit an isomorphy bordering on identity. I then endeavoured to explain the similar molecular structure of these two substances by referring to the analogy of the (CH_3)-group and Br-atom in the positions 1 and 2, particularly in a *spacial* respect. The small differences in crystalline form, melting point etc., are then caused by the difference which of course exists between CH_3 and Br.

We may now inquire how matters will be in both molecules as regards the substitution of the two remaining H-atoms of the core for instance. It is interesting to notice that as regards the substitution by (NO_2) the two H-atoms in each of the two isomers are quite *equivalent* and — what is still more striking — that this substitution does not perceptibly alter the molecular symmetry of the two molecules, so that *the crystallographical relation of the initial products is preserved in the substitution derivatives.*

If we nitrate the 1-2-4-6-tribromotoluene with nitric acid of 1,52 sp. gr. a dinitro-product is obtained, as shown by NEVILE and WINTHER [1]).

WROBLEWSKY [2]) had previously obtained a mono-nitro-derivative which differs in its melting point but little from the dinitro-product.

But notwithstanding many efforts, I have never, succeeded in obtaining a mononitro-compound not even as a bye-product, when using fuming nitric acid.

The mere formula of 1-2-3-5-*tribromotoluene* does not at once raise a suspicion that a dinitro-product will be formed in this case. If, however, the analogy of (CH_3) in the position 1 and Br in the position 2 is really so great that the difference amounts almost to nothing, we may surmise that the 1-2-3-5-*tribromotoluene* will behave on nitration also nearly quite analogously to the other isomer. The experiment shows that in this case also not a trace of any mononitro-derivative is obtained; we obtain exclusively a *dinitro*-product, which is in all respects quite analogous with the above named *dinitro*-derivative.

After nitration by red fuming nitric acid (sp. gr. 1,516 at 16°) in the cold, separation by adding an excess of water, agitation with benzene and ether and recrystallisation from *benzene*, in which both isomers are very soluble, the two substances are at once obtained pure in large colorless or pale sherry-colored crystals, whose bromine-amount corresponds with that of the dinitro-derivative.

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1) NEVILE and WINTHER, Journ. Chem. Soc. Vol. 37. 438; Berl. Ber. 13. 974.

2) WROBLEWSKY, Ann. d. Chemie 168. 147.

The 1-2-4-6-*tribromo*-3-5-*dinitro-toluene* melts at 220° ; the 1-2-3-5-*tribromo*-4-6-*dinitro-toluene* at 210°.

Like the two *tribromotoluenes* themselves, these substances are again quite *isomorphous* and owing to peculiar twin-formation, they so resemble each other, that at first sight we cannot distinguish the two kinds of crystals from each other.

a. 1-2-4-6-*tribromo*-3-5-*dinitro-toluene*.

$$C_6 \underset{(6)}{Br} . \underset{(4)}{Br} . \underset{(2)}{Br} . \underset{(5)}{(NO_2)} . \underset{(3)}{(NO_2)} . \underset{(1)}{(CH_3)} ;$$ melting point 220°.

From benzene this substance crystallises in large apparently quadratic, colorless crystals which are nearly all *twins*, — which may be recognised at once by a very fine diagonal on two of the broadest planes. We also may obtain needle shaped or very elongated thick pillar shaped crystals. The planes are generally angular and give plural
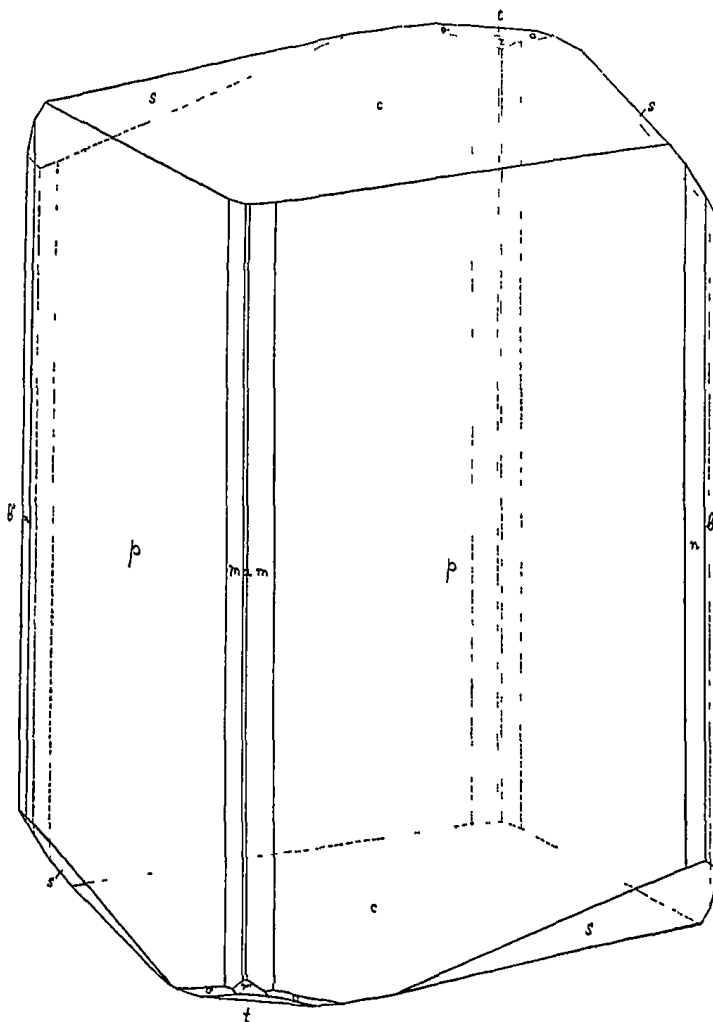

Fig. 1.

reflexes. The crystals are also frequently bordered by curved planes and by vicinal forms in the prism-zone. These circumstances render an accurate investigation very difficult; occasionally, however, I obtained better formed crystals, which gave very sharp reflexes and served for the following accurate measurements.

They are *monoclino-prismatic* with the axial relation ·

$$a : b : c = 0,5217 : 1 : 0,7803$$
$$\beta = 85°12'.$$

Forms observed are: $m = \{110\}$ and $p = \{120\}$, broad and lustrous; $a = \{100\}$ and $n = \{130\}$, very narrow; a is generally hazy; $b = \{010\}$, a little broader, but is generally absent; $c = \{001\}$, large and very lustrous; $r = \{\bar{1}01\}$, well developed and lustrous; $t = \{\bar{1}04\}$, narrower and is often absent; $o = \{\bar{1}12\}$, generally small and dull, occasionally a little broader and better reflecting; $s = \{\bar{1}32\}$, large and lustrous, but generally there are only two parallel planes present.

Combinations of *all* the forms rarely occur. Generally such with m, p, c, r; m, p, b, c, r, t, s and o; m, p, a, b and c, etc. The more typical crystals are shown in figures 1-3.
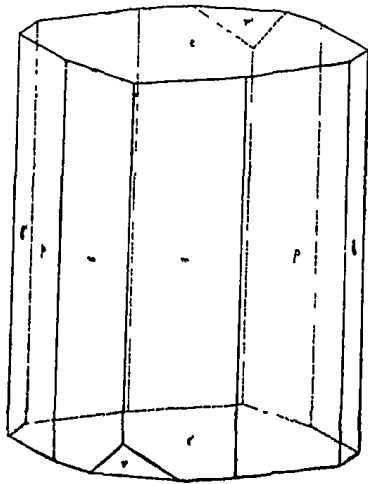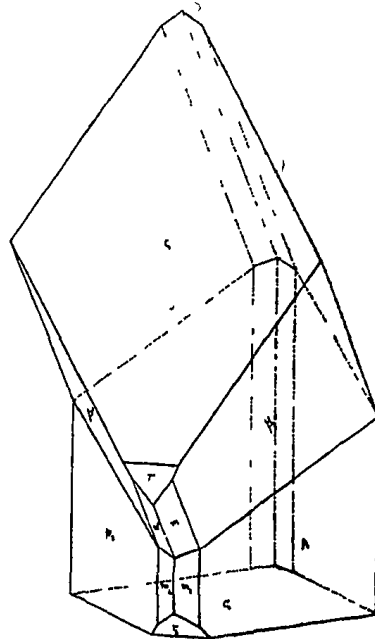

Fig. 2.   Fig. 3.

In the properly formed crystals, the angular values are very constant; the reflexes are as sharp as possible. The substance has a decided tendency to twin-formation; in this, one form $\{102\}$ is a

twin-plane with a twin-axis normally standing on it. On the plane of p may be often observed a delicate line parallel $p : c$; in this vertical zone the most important geometrical anomalies are found.

The following are the calculated and observed angular values.

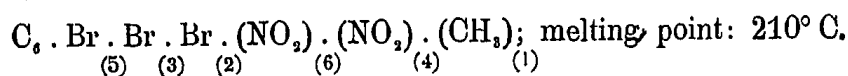|	Observed:	Calculated:
$^*m : m = (110) : (1\bar{1}0) =$	$54° 56^1/_2{}'$	—
$m : a = (110) : (100) =$	$27\ 28^1/_4$	$27° 28^1/_4{}'$
$m : r = (110) : (\bar{1}01) =$	$43\ 20$	$43\ 13$
$^*c : r = (001) : (\bar{1}01) =$	$59\ 39$	—
$r : a = (\bar{1}01) : (\bar{1}00) =$	$35\ 20$	$35\ 33$
$c : a = (001) : (100) =$	$85\ 15$	$85\ 12$
$^*c : m = (001) : (110) =$	$85\ 44^1/_2$	—
$c : p = (001) : (120) =$	$86\ 40$	$86\ 36$
$c : n = (001) : (130) =$	$87\ 30$	$87\ 25$
$c : b = (001) : (010) =$	$89\ 58$	$90\ \ 0$
$p : n = (120) : (130) =$	$11\ 12$	$11\ 13$
$m : p = (110) : (120) =$	$18\ 35$	$18\ 39$
$p : r = (\bar{1}20) : (\bar{1}01) =$	$55\ 25$	$55\ 29$
$c : t = (001) : (\bar{1}04) =$	$21\ 12$	$21\ \ 2$
$c : o = (001) : (\bar{1}12) =$	$41\ 52^1/_2$	$41\ 52$
$c : s = (001) : (\bar{1}32) =$	$55\ 49$	$55\ 54$
$m : s = (\bar{1}\bar{1}0) : (\bar{1}32) =$	$47\ 36^1/_2$	$47\ 35^1/_2$

A distinct cleavability was not observed.

On c, r, and a the position of the optical elasticity-axis is orientated perpendicularly to the direction of the orthodiagonal; the symmetrical angle of extinction on m amounts to $23°$ with regard to the vertical axis. An axial image could not be observed.

The sp. gr. of the crystals is 2,456 at 15°; the equivalent volume is, therefore : 170,6.

The topical axes are:

$$: \psi : \omega = 3,9087 : 7,4921 : 5,8461.$$

b. 1-2-3-5-*tribromo*-4-6-*dinitrotoluene*.

$C_6 . Br . Br . Br . (NO_2) . (NO_2) . (CH_3)$; melting point: 210° C.
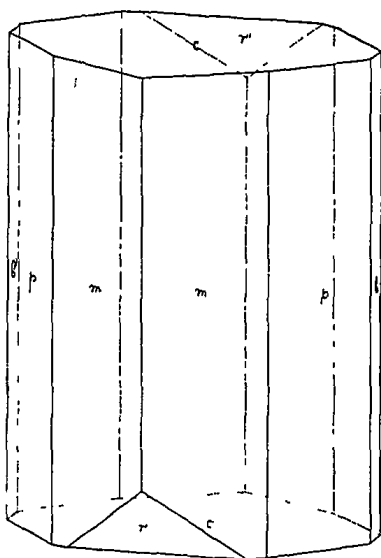   (5) (3) (2)   (6)   (4)   (1)

Fig. 4.

This compound crystallises from benzene in very large, colorless, iso-metrical-developed crystals, which are always twins and of exactly the same form as that of the previous compound with which this substance is isomorphous.

The geometrical anomalies caused by the curvature or angulation of the planes are more considerable with this derivative, than with the previous one; the development of the crystals is less perfect and they also exhibit a smaller number of combining forms. From ether and\ acetone we obtain besides twin-crystals also single needles which can be measured more accurately.

The symmetry is *monoclino-prismatic*; the axial relation is:

$$a : b : c = 0,5392 : 1 : 0,7574.$$

$$\beta = 86°28'.$$

Forms observed are: $m = \{110\}$ and $p = \{120\}$, broad and lustrous; $c = \{001\}$, very lustrous and well developed; $r = \{\bar{1}01\}$, smaller but properly measurable; $b = \{010\}$, narrow and often absent. Angular values:

		Observed:	Calculated:
*p : p = (120) : (1\bar{2}0) =		94°13'	—
*p : c = (120) : (001) =		87 35$^1/_2$	—
*p : r = (\bar{1}20) : (\bar{1}01) =		56 53$^1/_2$	—
p : m = (120) : (110) =		18 50	18°49'
m : m = (110) : (1\bar{1}0) =		56 54	56 36
m : r = (\bar{1}10) : (\bar{1}01) =		44 57	45 2
c : r = (001) : (\bar{1}01) =		57 6	56 55
m : c = (110) : (001) =		86 59	86 52$^1/_2$

A distinct cleavability was not observed.

This substance also has a decided tendency to twin-formation towards $\{102\}$ as twin-plane; single crystals are rare. Owing to this peculiarity, the external resemblance of this isomer with the former is increased in a high degree. It should be observed that these twins and also those of the former substance often also show $\{010\}$ and

symmetrical vertical lines on the prism p, with regard to the twin-section. The sp. gr. of a perfectly homogenous fragment of a crystal was found to be 2,465 at 15°; the equivalent-volume is therefore 169,98 and the topical axes become:

$$\chi : \psi : \omega = 4,0286 : 7,4713 : 5,6580.$$

I have tried, of course, to gain some insight into the progressive course of the binary meltingpoint-line of these two isomorphous derivatives, although the want of sufficient supply of material proved a great obstacle.

This investigation had, however, soon to be abandoned because the mixtures of the two substances assuming a much darker colour are decomposed at their melting point with violent evolution of gas; the temperatures are situated between 210° and 220°. The more the mixture contains of the compound with the higher melting point, the more readily the decomposition takes place, and therefore the only mixtures of which I could sharply determine the melting point, were those containing from $0°/_0$ to $44^{1}/_{2}°/_0$ of the derivative with the higher melting point; this melted at 214°, the others between 210° and 214°. I, therefore, suspect that we have here a continuous melting curve; whether an absolute maximum occurs in the meltingpoint-line, such as happens with the two non-nitrated initial products, could not be decided. The mutual behaviour of these two isomorphous derivatives probably corresponds entirely with that of the two tribromotoluenes.

From mixed solutions of the two nitro-derivatives in benzene we obtain large curve-planed and badly formed mixed crystals which exhibit the same typical twin formation as the two components, but which generally possess only {110}, {120} and {001}. They are unsuitable for measuring purposes.

c. 1-3-4-5-*tribromo-2-6-dinitro-toluene.*

$$C_6 . Br . Br . Br . (NO_2) . (NO_2) . (CH_3) \quad ; \quad \text{melting point:} \quad 216° C.$$
$$ (5) (4) (3) (6) (2) (1)$$
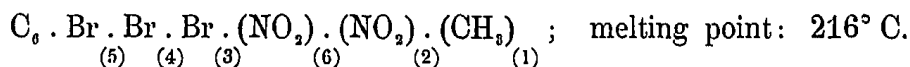
When recrystallised from benzene, in which this compound, which was prepared in the same manner as the preceding ones, is less soluble at the ordinary temperature than the two other isomers, the substance is obtained in thick, quadratically-bounded, crystalline plates, which at first sight appear tetragonal, an occurrence to be expected, when taking into account the slight morphotropical force of the (NO_2)-group, and the previously found tetragonal symmetry of the corresponding tribromotoluene.
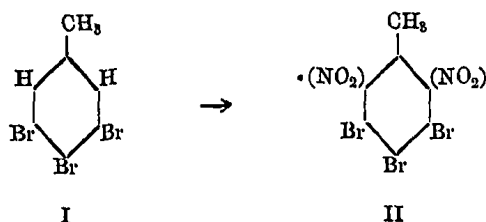
The investigation, however, soon showed that the symmetry is *not* tetragonal, and I first thought I had before me a monoclinic compound, — certainly with plenty of geometrical anomalies, — but still reasonably conforming to all the requirements of the monoclinic symmetry. This would also have agreed with everything that I have formerly communicated as to the formrelation of tetragonal and monoclinic crystals.

I hesitated a long time before I could give up this last idea, particularly because the measurement of a very large number of crystals taught me, that in this case just as with the two former compounds, the peculiar softness of the substance causes geometrical disturbances of the crystals during the crystallisation, and because the axial elements of this compound when assuming the monoclinic symmetry exhibited an analogy bordering on isomorphy with those of the two investigated isomers.

The deviations of the angles from the values required for the monoclinic symmetry appeared however, to be so systematical, that there could be no longer a doubt as to the *triclinic* symmetry of these remarkable crystals, even though they were found to represent a *monoclinic limit-form.*

Afterwards, I have also been able to find exceedingly small deviations in the optical orientation of the directions of extinction which again corroborated my belief, that triclinic crystals of a pseudo-monoclinic form are present here. This makes us feel convinced that even if the morphotropical force of the *single* (NO_2) group is generally feeble *two* such groups may cause a comparatively *strong* deformation of the crystal-molecule; and also that the spacial structure of the benzene derivatives is not fully explained by the usual formulation of these substances. For the ordinary schematical manner of writing alone does not explain why a compound of the type 1 should have another symmetry than one of the type II, — even though, owing to the occurrence of the pseudo-monoclinic *limit-form*, the close relation of the two kinds of symmetry is in each case very plainly perceptible :
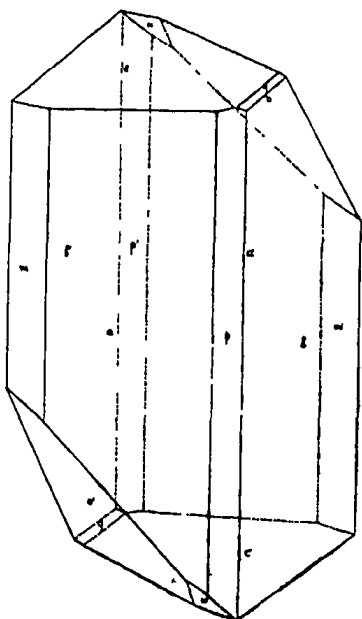

I   II

Fig. 5.

The crystals of the 1-3-4-5-*tribromo-2-6-dinitro-toluene* are represented in Fig. 5 in the form in which they crystallise from a mixture of carbon disulphide and benzene. The quadratical looking plate-like crystals, deposited from benzene only, exhibit nearly the same forms; in their case, however, the form a is very predominating; then follows c, whilst the other forms are narrow and little developed; moreover the form q is always and o often absent. I also occasionally obtained from benzene, thick prismatic crystals with a, b and c and even o.

Triclino-pinacoïdal. The axial relation is:

$$a : b : c = 0,5322 : 1 : 0,9581$$

$a = 88°21'$.	$A = 88°26'$.
$\beta = 95° 4'$.	$B = 95° 2'$.
$\gamma = 90°58'$.	$C = 90°50'$.

Forms observed are: $a = \{100\}$, and $b = \{010\}$ equally strongly developed, a generally more lustrous than b; $c = \{001\}$ very lustrous; $o = \{\bar{1}22\}$ well developed and lustrous; $\omega = \{\bar{1}12\}$ smaller than o but very lustrous; $q = \{012\}$, small and less conspicuous; $m = \{\bar{1}10\}$, narrow, but broader than $p = \{110\}$, which form is often present with a single plane; $s' = \{\bar{3}44\}$ very narrow and not properly measurable [1]).

			Observed:	Calculated:
*a :	$b = (100) : (010) =$	89°10′	—
*a :	$c = (100) : (001) =$	84 58	—
*b :	$c = (010) : (001) =$	91 34	—
*o :	$a = (\bar{1}22) : (\bar{1}00) =$	59 35	—
*o :	$c = (\bar{1}22) : (001) =$	55 25½	—
a :	$p = (100) : (110) =$	27 32	27°45½′
a :	$m = (100) : (1\bar{1}0) =$	28 7	28 7

[1]) If, in view of the symbol of s' we rather choose $o = \{\bar{2}43\}$, $\omega = \{2\bar{2}3\}$ $s' = \{\bar{3}43\}$, whilst retaining the other symbols, we get $a : b : c = 0,5322 : 1 : 0,7186$, which agrees better with the other two isomers,

		Observed.		Calculated.	
$b : o = (010) : (\bar{1}22) =$	54	33	54	34
$b \cdot m = (0\bar{1}0) : (1\bar{1}0) =$	62	40	62	51
$b : p = (010) : (110) =$	61	33	61	$24^{1}/_{2}$
$c : q = (001) : (012) =$	26	5	25	50
$b : q = (010) : (012) =$	65	39	65	49
$o : m = (\bar{1}22) : (\bar{1}10) =$	43	21	43	39
$o : s' = (\bar{1}22) : (\bar{3}44) =$	11	52 (circa)	12	8
$\omega : b = (\bar{1}12) : (0\bar{1}0) =$	108	$49^{1}/_{2}$	108	47
$\omega : o = (\bar{1}12) : (\bar{1}22) =$	16	51	16	39
$\omega : c = (\bar{1}12) : (001) =$	48	$1^{1}/_{2}$	48	$0^{1}/_{2}$
$\omega : m = (\bar{1}12) ; (\bar{1}10) =$	47	30	47	$13^{1}/_{2}$
$a : \omega = (\bar{1}00) : (\bar{1}12) =$	53	35	53	$35^{1}/_{2}$
$a : q = (100) : (012) =$	85	37	85	55
$\omega : q = (\bar{1}12) : (012) =$	40	35	40	$30^{1}/_{2}$
$q : o = (012) : (\bar{1}22) =$	38	56	38	54
$m : c = (1\bar{1}0) : (001) =$	84	47	84	$45^{3}/_{4}$
$p : c = (110) : (001) =$	86	22	86	19

The position of the optical elasticity-axis on a was determined by means of a very thin lamelle, with the aid of a BERTRAND Quartz-Ocular, and found to be 4° with the side (100) : (010); on b the angle amounts to more than 45° with respect to the side (110) · (010). An axial image could not be observed.

By means of a THOULET's solution, the sp. gr. of the crystals was found to be 2,459 at 17°; the equivalent volume is, therefore, 170,39, and the topical axial relation becomes:

$$\chi : \psi : \omega = 3,6982 : 6,9496 : 6,6584.$$

The close relation of this triclinic derivative with the two monoclinic isomers is therefore obvious That there is still an essential difference in the nature of the molecular orientation, which in these three cases determines the crystalline structure, is also shown by the fact, that the first two derivatives exhibit a decided tendency to a similar and typical twin-formation, which is utterly absent in the latter isomer.

I will give lateron some information as to the other nitro-products of the isomeric tribromotoluenes, as these have not as yet been obtainable in measurable crystals.