Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

*Citation:*

F.M.Jaeger, On the Tri-para-Halogen-Substitution products of Triphenylmethane and thriphenylcarbinol, in:
KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 789-798

With the oscillations of long duration that inaccuracy in the registration does of course not appear.

So we come to the conclusion *that the oscillations of short and of long duration of the magnetic force at Batavia and at Buitenzorg have the same ratio of amplitude and that they therefore cannot be caused, or only for a small part, by the current running through the outer crust of the earth.*

By far the greater part of the influence of the earth-currents must therefore come from currents at greater depths and of greater extension, and more equal in intensity.

**Chemistry.** — *"On the Tri-para-Halogen-Substitution-Products of Triphenylmethane and Triphenylcarbinol."* By Dr. F. M. Jaeger. (Communicated by Prof. A. P. N. Franchimont).

(Communicated in the meeting of March 28, 1908).

§ 1. Some years ago, I investigated [1]) crystals of *Tri-p-Chloro-Triphenylmethane*, from different preparations which had been obtained by Dr. P. J. Montagne in two different ways, namely from *p*-leuca-niline by diazotation and subsequent introduction of the three chlorine atoms and from tetrachlorobenzopinacoline by intramolecular rearrangement.

I then gave a detailed description of the remarkable optical behaviour of the compound in convergent polarised light and endeavoured to elucidate the same by a coloured figure.

Wishing to extend this research also to the other halogen-derivatives, I have first of all prepared the tribromoderivative of *p*-leu-caniline by the method proposed by O. Fischer and W. Hess. [2]) Afterwards I received from Prof. Fischer a small quantity of each of the three halogen derivatives, which enabled me to prepare the three corresponding trihalogen-carbinols by oxydation with chromic acid in acetic acid solution, so that these three substances could be included also in this investigation. I will not omit to thank this savant once more for his kind assistance.

Of *Tri-p-Bromotriphenylmethane* [3]) I gave a description a short time ago in the Zeits. f. Kryst. **44**, 57—58. (1907). The habit of the crystals is quite analogous to that of the chloro-compound; they are more compact of form and generally much larger, but at the same time they·cannot be measured so accurately, owing to a curving

---

[1]) Receuil **24**. 124, 131. (1905).

[2]) O. Fischer und W. Hess, Berl. Ber. **38**. 336. (1905).

[3]) F. M. Jaeger, Zeits. f. Kryst. und Miner. Bd. **44**. 57. (1907).

of the planes. Nevertheless the complete isomorphism with the chloro-compound may be clearly shown, of course the differences are somewhat larger than in the case of isomorphous substitution products in which one atom only is replaced by another and not three at the same time, as is the case here.

§ 2. In the following the crystalforms of the diverse substitution-products are described.

**Tri-p-Jodotriphenylmethane.**

$(C_6 H_4 J)_3 : CH$; m. p. 132° C.

This compound was kindly presented to me for investigation by prof. O. FISCHER of *Erlangen*.



Fig. 1.

Tri-p-Jodotriphenylmethane.

From ligroïn it crystallises in small, refractive, pale yellow needles which are readily measurable. From benzene, however, a *double compound* containing benzene crystallises in large transparent prisms. The chloro- and bromo-compounds, however, do *not* unite with benzene; from the benzene solution the crystals of the pure compounds are always deposited.

*A. Tri-p-Jodotriphenylmethane*, from ligroïn.

The symmetry is *rhombic-bipyramidal*; the axial ratio is calculated as:

$$a : b . c = 0,5765 : 1 : 0,8798.$$

Evidently this substance is directly isomorphous with the *Cl* and the *Br*-compound although here the differences are again more considerable than usual on account of the simultaneous substitution of *three* isomorphogeneous atoms.

Forms observed : $m = \{110\}$, well developed and lustrous; $a = \{100\}$, very narrow and dim; $q = \{011\}$, yielding good reflexes; $p = \{130\}$, very narrow and dull.
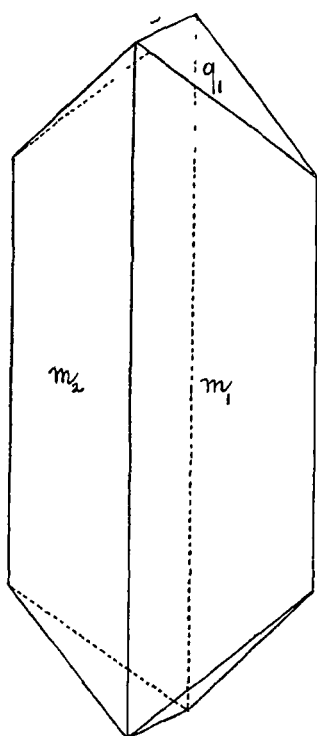
| Angular values : | Measured : | Calculated : |
|---|---|---|
| $m : m = (110) : (1\bar{1}0) =$ | ⊦59° 55¹/₂' | — |
| $m : q = (110) : (011) =$ | 70° 30¹/₂' | 70° 44¹/₂' |
| $q : q = (011) : (011) =$ | ⊣82° 41' | — |
| $m : q = (110) : (130) =$ | 30° 15' | 30° 30' |

Distinctly cleavable along $m$.

The optical axial plane for *all* rays is {001}; the *a*-axis is the first bisectrix with positive character. Average strong, rhombic dispersion, with $\varrho > v$; the apparent axial angle in cedar-oil (1,54) is about 68°.

The sp. gr. of the crystals is 2,141 at 15°; the equivalent volume 290,64.

Topic parameters : $\chi : \psi : \omega = 4,7883 : 8,3061 . 7,3077.$

### B. Tri-p-Jodotriphenylmethane + 1 Benzene.

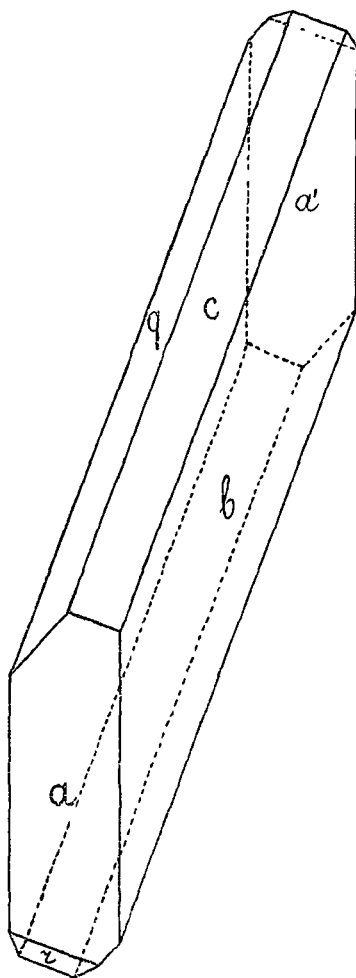Large, very lustrous and transparent crystals.



Fig. 2.
Tri-p-Jodo-Triphenylmethane + 1 Benzene.

When taken out of the motherliquor they keep transparent for a fairly long time but after a few hours they lose all their benzene while retaining their form; sometimes there is only a partial loss. It is not improbable that the amount of benzene varies with the temperature and pressure.

The symmetry is *triclino-pinacoidal*. Axial ratio:

$$a : b : c = 0{,}5719 : 1 : 1{,}4298.$$

$$A = 101° 12' \qquad \alpha = 109° 8'$$
$$B = 123° 15' \qquad \beta = 126° 21'$$
$$C = 98° 5' \qquad \gamma = 107° 32'$$

Forms observed: $b = \{010\}$, very predominant and lustrous; $c = \{001\}$ and $a = \{100\}$, well developed and yielding sharp reflexes; $q = \{0\bar{1}1\}$, also rather largely outgrown; $r = \{\bar{1}02\}$, narrow but readily measurable.

The habit is flattened towards $\{010\}$ but° elongated along the $a$-axis. Perfect cleavage parallel $\{010\}$.

| Angular values: | Measured: | Calculated: |
|---|---|---|
| $a : b = (100) : (010) = {}^*98°\ 5'$ | | — |
| $c : b = (001) : (010) = {}^*78°\ 48'$ | | — |
| $c : a = (001) : (100) = {}^*56°\ 45'$ | | — |
| $a : r = (100) : (10\bar{2}) = {}^*50°\ 10'$ | | — |
| $b : q = (010) : (01\bar{1}) = {}^*44°\ 4'$ | | — |
| $a : q = (100) : (01\bar{1}) = 106°\ 8^{1}/_{2}'$ | | |

The ratio of the axes $a$ and $b$ in the two derivatives is quite analogous.

In accordance with the supposition of a varying benzene percentage the angular values of the individual crystals vary rather considerably.

§ 3. When we compare the three *para*-substituted trihalogen-compounds of triphenylmethane with each other, there can be no doubt as to the analogous molecular structure of the derivatives in the solid condition. Only in *optical* orientation the *chloro*-compound distinctly differs:

| *Tri-p-Chloro-compound*: Rhombic-bipyramidal. | *Tri-p-Bromo-compound*: Rhombic-bipyramidal. | *Tri-p-Iodo-compoun* Rhombic-bipyramid. |
|---|---|---|
| Forms: | Forms: | Forms: |
| $\{110\}; \{011\}; \{010\}; \{130\}; \{012\}; \{102\}$ | $\{110\}; \{011\}; \{010\}; \{102\}$ | $\{110\}; \{011\}; \{13$ |
| $a : b : c = 0{,}5904 : 1 : 0{,}9261.$ | $a : b : c = 0{,}5896 : 1 : 0{,}9003.$ | $a : b : c = 0{,}5765 : 1 : 0{,}\mathcal{E}$ |
| Cleavable towards $\{110\}$. | Cleavable towards $\{110\}$. | Probably cleavable wards $\{110\}$. |
| Thick-prismatic towards the $c$-axis. | Short-prism. tow. the $c$-axis | Elongated prisms tow the $c$-axis |
| $(110) : (1\bar{1}0) = 61°\ 7'$ | $(110) : (1\bar{1}0) = 61°\ 3'$ | $(110) : (1\bar{1}0) = 59°\ 55$ |
| $(110) : (011) = 69°\ 47^{1}/_{2}'$ | $(110) : (011) = 70°\ 8'$ | $(110) : (011) = 70°\ 44$ |
| $(011) : (01\bar{1}) = 85°\ 36'$ | $(011) : (0\bar{1}1) = 83°\ 59^{1}/_{2}'$ | $(011) : (0\bar{1}1) = 82°\ 41$ |
| Sp. Gr. $= 1{,}435$; | Sp. Gr. $= 1{,}752$; | Sp. Gr. $= 2{,}141$; |
| Equiv. Vol. 242,16. | Equiv. Vol. 274,54. | Equiv. Vol.: 290,6 |

| Chief dimensions of the crystal ;ructure.<br>:$\psi:\omega = 4,5004:7,6225:7,0593.$ | Chief dimensions of the crystal structure $\chi:\psi:\omega =$<br>$= 4,7327:8,0270:7,2267.$ | Chief dimensions of the crystal structure $\chi:\psi:\omega =$<br>$4,7883:8,3061:7,3077.$ |
|---|---|---|
| Optical orientation :<br>The axial plane for *violet, blue* nd *green* is {001} but for the *range* and *red* rays it is, however )10}. The first diameter for all )lours is the $a$-axis of — charac- :r. The axial angle for *violet* is early 0°. | Optical orientation :<br>For *all* colours the axial plane {001}.<br>The first bisectrix is the $a$-axis of + character. Weak dispersion : $\varrho > v$. The apparent axial angle in cedar-oil is about 50°. | Optical orientation :<br>For *all* colours the axial plane is {001} with the $a$-axis as first diameter of + character.<br>Middlemost dispersion: $\varrho > v$.<br>The apparent axial angle in cedar-oil is about 70°. |

It should, however, be remarked that this *Tri-p-Chlorotriphenylmethane* exhibits also a very interesting optical variability as will be noticed from the subjoined observations :

*a*. Crystals from O. FISCHER; the compound is recrystallised from petroleum-ether (b.p. 40°—60°).

For *all* colours the optical axial plane was: {010}. Very strong dispersion: $\varrho > v$; the $a$-axis, is the 1st diameter and possesses a negative character. The apparent axial angle in olive-oil is very small and amounts to about 5°.

With other crystals, particularly the thicker prisms, I found that the axial plane for violet and blue rays is {001} but for *all* other colours {010}; the $a$-axis, is the first bisectrix, but now of a positive character; the very strong dispersion was: $\varrho >$ green.

Other little crystals only exhibited the *violet* in {001}, and the *blue, green, red, yellow* etc. in the plane {010}.

*b*. Crystals from the collection of the Organic Chemical Laboratory at *Leiden*, prepared by P. J. MONTAGNE. *They were optically perfectly identical with the crystals which I examined previously.* [1] Some of the crystals had become opaque but had retained their form. This fact is already mentioned by MONTAGNE [2] who observes also that the meltingpoint remains practically unaltered.

At my request Dr. MONTAGNE forwarded me some powder of *Tri-p-Chlorotriphenylmethane* from tetrachlorobenzopinacoline, which after recrystallisation from petroleum ether showed the following properties:

The axial plane for *all* colours is now {001}. Very strong dispersion: $\varrho > v$; the $a$-axis is the 1st bisectrix; the apparent axial angle

---

[1] Zie Receuil d. Trav. d. Chim. d. Pays-Bas, **24**. 124, 131. (1905).

[2]. loco cit. p. 122.

in olive-oil is much larger than in the first case and amounts to about 10°.

Recrystallisation from petroleum-ether does not alter the properties of a definite crystal species; all preparations, however have the same meltingpoint and a complete identical crystalform.

We are therefore confronted with the fact that the compound $CH(C_6H_4Cl)_3$, m. p. 92° occurs, under varying circumstances, in forms which cannot be distinguished by chemical and crystallographical means, but whose *optical orientation is very different*. Sometimes, the crystals show a positive, sometimes a negative double refraction; one crystal shows a crossing of the axial planes for diverse colours, another for only a single colour; others again for no colour whatever, the axial plane then being either {001} or {010} whilst the dispersion is sometimes : $\varrho > v$, sometimes $\varrho < v$.

Of course, the possibility is not excluded that exceedingly small traces of foreign impurities cause this change of the so sensitive optical orientation. The result of the investigation of *Tri-p-Chlorocarbinol* showing its complete isomorphotropic relation to the said derivative, renders it not improbable that a trifling admixture of this oxidationproduct is the cause of the phenomenon.

In accordance with this is the fact, communicated to me privately by Dr. MONTAGNE, that a turbidity of the transparant crystals *never* occurs with the thin *rapidly* formed needles, but always with the thick and short crystals of *Tri-p-Chlorotriphenylmethane*, obtained by *slow* crystallisation.

But it is also conceivable that such large molecules as that of *Tri-p-Chlorotriphenylmethane* might in different circumstances suffer small deviations of their average atomistic configuration, which cannot be demonstrated chemically or crystallographically, but which can be shown optically.

Of late years numerous investigations have been carried out which must lead to the conclusion, that many properties of crystallised matter such as the growth- and cohesion-phenomena must be contributed to the regular molecular aggregation, whereas other ones such as the *optical* properties would have their origin, at least to a great extent, in the properties of the molecules themselves. This view is strengthened by different observations made with the so-called liquid crystals and doubly-refracting liquids; also by some experiments made by WALLÉRANT a.o. on the optical behaviour of deformed solid crystals. And phenomena like those observed here with *Tri-p-Chloro-Triphenylmethane* may show that it is possible that the spacial configuration of the chemical molecules is variable within

narrow limits. I believe I have noticed something similar some time ago with a specimen of the *Dibromide* of 1-3-5 *Hexatriene* presented to me by Prof. VAN ROMBURGH[1]). Notwithstanding the identical crystal form the preparation made by addition of bromine to the hydrocarbon showed slight optical differences with that prepared from divinylglycol by means of $PBr_3$.

And although I will not as yet venture to give a decision one way or other, I fancy that on account of the phenomena described here the matter is of sufficient importance to be brought to the notice of chemists.

### § 4. Tri-p-Chloro-Triphenylcarbinol.

$$(C_6H_4Cl)_3 : C\text{-}OH : \text{m.p. } 98° \text{ C.}$$
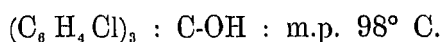
Crystallises from ethyl alcohol in colourless, strongly refracting needles, also from ether $+$ ligroïn. The crystals possess great lustre and are well constructed.

Rhombic-bipyramidal.

$$a : b : c = 0,6009 : 1 : 0,9781.$$

Forms observed: $m = \{110\}$, yields ideal reflexes; $q = \{011\}$, also yielding irreproachable images; $b = \{010\}$ and $p = \{210\}$, narrow but easily measurable. The habit of the crystals is elongated towards the $c$-axis. Crystals from ethylalcohol are short prismatic and still exhibit the forms $o = \{133\}$ and $s = \{102\}$, generally reflecting badly.
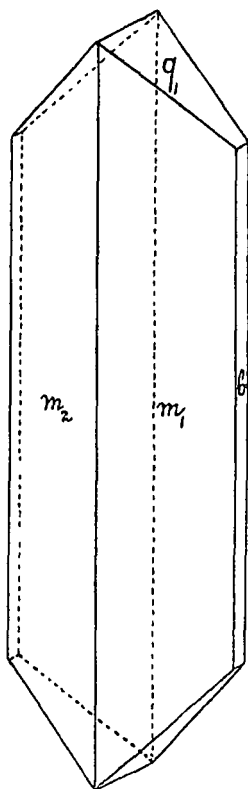


Fig. 3.
Tri p-Chloro-Triphenyl-carbinol.

| | Measured : | Calculated : |
|---|---|---|
| $m : q = (110) : (011) =$ | *68° 53½' | — |
| $m : b = (110) : (010) =$ | *59° 0' | – |
| $m : m = (110) : (\bar{1}10) =$ | 62° 1' | 62° 0' |
| $q : b = (011) : (010) =$ | 45° 46½' | 45° 38' |
| $q : q = (011) : (0\bar{1}1) =$ | 88° 36½' | 88° 44' |
| $b : p = (010) : (210) =$ | 42° 27' | 42° 16²/₃ |
| $p : m = (210) : (110) =$ | 16° 47½' | 16° 43¹/₃. |

---

[1]) Compare Trans. Chemic. Soc. (1908) p. 517—524.

No distinct cleavage was found.

The optical axial plane is {001}, with the $a$-axis as a first bisectrix of positive character. Weak dispersion: $\varrho > v$. The apparent axial angle in olive oil amounts to about 55°.

The sp. gr. of the crystals is: 1,423; the equivalent volume 255,44.

Topic parameters. $\chi : \psi : \omega = 4,5516 : 7,5748 : 7,4089$.

A comparison with *tri-p-chlorotriphenylmethane* shows that the morphotropic relations of both compounds are of such a nature that they border on *isomorphism*. In fact, both compounds form mixed crystals with each other.

## § 5. Tri-p-Bromo-Triphenylcarbinol.

$(C_6 H_4 Br)_3 : C.OH$; m.p. 133° C.

Crystallises from ethylalcohol in small colourless, clear crystals possessing a high lustre and a good geometrical construction.

Rhombic-bipyramidal.

$$a : b : c = 0,8407 : 1 : 0,8081.$$

Forms observed: $m = \{110\}$, predominant and yielding sharp reflexes; $a = \{100\}$ narrow but easily measurable; $q = \{011\}$, gives excellent reflexes and is well developed; $r = \{101\}$ small and somewhat dull. The crystals from alcohol are shown in fig. 4.
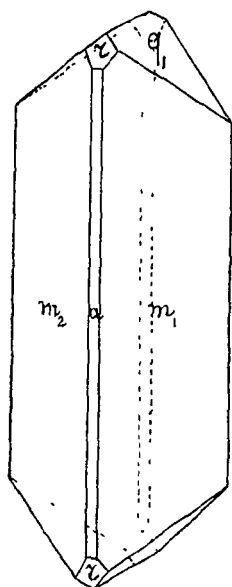


Fig 4.
Tri-p-Bromo-Triphenyl-
carbinol.

| Angular Values : | Measured : | Calculated : |
|---|---|---|
| $m : a = (110) : (100) =$ | ⁻40°  3¹/₄' | — |
| $m : q = (\bar{1}10) : (0\bar{1}1) =$ | ⁻66°  8¹/₂' | — |
| $q : q = (011) : (0\bar{1}1) =$ | 77° 52' | 77° 53' |
| $m : m = (110) : (1\bar{1}0) =$ | 80°  7¹/₂ | 80°  7¹/₂' |
| $m : r = (110) : (101) =$ | 57° 59' | 57° 58' |
| $r : q = (101) : (0\bar{1}1) =$ | 55° 50¹/₂ | 55° 53¹/₂' |
| $r : r = (101) : (10\bar{1}) =$ | 87° 45' | 87° 44' |
| $r : a = (101) : (100) =$ | 46°  7¹/₂' | 46°  8' |

No distinct cleavage.

The optical axial plane is {001}; the $b$-axis is the first bisectrix and of a negative character. The apparent axial angle in olive-oil is about 65°. No strong dispersion: $\varrho > v$.

The sp. gr. of the crystals is 1,847; the equivalent volume 269,08.

Topic parameters: $\chi : \psi : \omega = 6,1739 : 7,3439 : 5,9346$.

In contrast to what was found with both chloroderivatives, tri-bromocarbinol shows no distinct form-relationship with tribromo-triphenylmethane [1]). The substitution of $H$ by $-OH$, however, appears to exert an influence on the equivalent volume which is of a nature opposite to that which causes the same substitution in the chloro-derivative.

### § 6. Tri-p-Iodo-Triphenylcarbinol.

$$(C_6 H_4 J)_3 : C-OH; \text{ m.p.} : 155° C.$$

Crystallises from ethylalcohol in fairly large yellowish crystals which, however, contain either no terminal planes at all or else strongly curved ones.

In any case the isomorphism with the previous compound may be easily proved.

<div style="text-align:center">

Rhombic-bipyramidal.

$$a : b : c = 0,8543 : 1 : 0,817.$$

</div>

Forms observed: $m = \{110\}$, predominant and highly lustrous; $a = \{100\}$ narrow and generally absent but always giving a good reflexion; $q = \{011\}$ distinctly developed but in most cases curved and only approximately measurable; $r = \{101\}$ was observed once or twice.

|  | Measured: | Calculated: |
|---|---|---|
| $m : m = (110) : (1\bar{1}0) = $ | $*81°$  $1'$ | — |
| $q : q = (011) : (0\bar{1}1) = $ | $*78$  $29$ | — |
| $a : m = (100) : (110) = $ | $40°$  $36^1/_2$ | $40°$  $30^1/_2{}'$ |
| $m : q = (110) : (011) = $ | $66$  $3^1/_2$ | $65$  $44^1/_3$ |
| $m : r = (110) : (101) = $ | $58$  $10$ | $58$  $18$ |

No distinct cleavage.

The optical axial plane is $\{001\}$ with the $b$-axis as first bisectrix. Particularly large dispersion: $\varrho > v$. The apparent axial angle in olive-oil amounts to about 80°.

The compound crystallises from benzene in combination with the solvent.

### B. Tri-p-Iodo-Triphenylcarbinol + Benzene.

This occurs in large, yellowish needles having a strong lustre but generally possessing no terminal planes. In the case of one single individual however a few angles were measured. No trace of efflo-rescence was noticed in the crystals.

---

[1]) There is no question of a direct isomoiphism. By exchanging the $a$- and $b$-axis we can find $a' : b' : c'$ $1,189 : 1 : 0,9612$; which (with double $a$-axis) somewhat resembles the values for the bromoderivative.

Triclino-pinacoidal.

$$a : b : c = 1,3991 : 1 : 1,6135$$

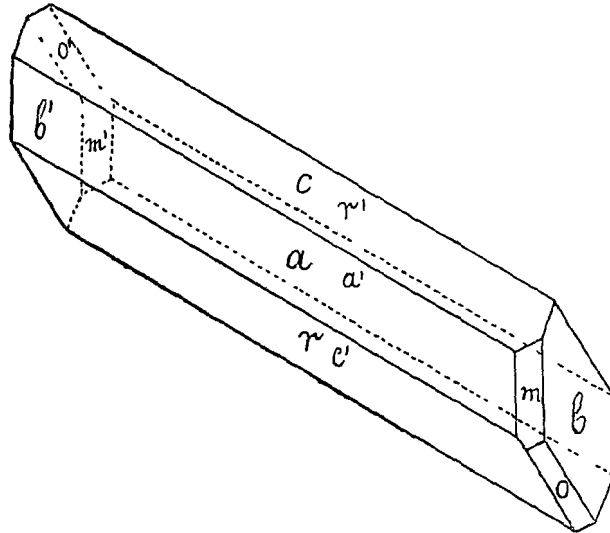| | |
|---|---|
| $A = 94° 12'$ | $a = 109° 16'$ |
| $B = 123° 10'$ | $\beta = 117° 36'$ |
| $C = 70° 4\frac{1}{2}'$ | $\gamma = 62° 52'$ |



Fig. 5.
Tri-p-Jodo-Triphenylcarbinol + 1 Benzene.

Forms observed $c = \{001\}$ and $a = \{101\}$, equally strongly developed, $r = \{\bar{1}01\}$, broader than $a$ and $c$ and very lustrous; $b = \{010\}$, well developed; $o = \{11\bar{1}\}$ and $m = \{110\}$, about equally large and giving a good reflexion.

The habit is elongated towards the $b$-axis. The ratio $b : c$ is practically twice that of the *Tri-p-Jodotriphenolcarbinol* itself.

| | |
|---|---|
| $a : c = (100) : (001) =^* 56°.50'$ | — |
| $c : r = (001) : (\bar{1}01) =^r 72\ 6$ | — |
| $c : b = (001) : (0\bar{1}0) =^* 94\ 12$ | — |
| $a : b = (100) : (0\bar{1}0) =^* 70\ 4\frac{1}{2}$ | — |
| $c : o = (001) : (1\bar{1}\bar{1}) =^* 80\ 22$ | — |
| $m : o = (\bar{1}\bar{1}0) : (1\bar{1}\bar{1}) = 39\ 22$ | $39\ .23\frac{1}{2}$ |
| $m : c = (\bar{1}\bar{1}0) : (00\bar{1}) = 60\ 2$ | $59\ .45$ |

No distinct cleavage.

On $\{\bar{1}01\}$ the extinction amounts to about $32\frac{1}{2}°$ in regard to the $b$-axis. Sp. Gz. 2,079 at 17°; Equiv. Vol. = 344,39.

Topic axes : $\chi : \psi : \omega = 8,4070 : 6,0090 : 9,6950$.

*Groningen,* March 1908.