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Crystallography. — "*Contribution to the knowledge of the isomorphous substitution of the elements Fluorine, Chlorine, Bromine and Iodine, in organic molecules*". By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of November 25, 1905).

Some time ago a paper was published by GOSSNER ¹⁾ on the crystal-forms of *Chlorobromonitrophenol*, *Dibromonitrophenol* and *Iodobromonitrophenol* being an experimental contribution to the knowledge of

¹⁾ B. GOSSNER, Krystallographische Untersuchung organischer Halogenverbindungen. Ein Beitrag zur Kenntniss der Isomorphie von Cl, Br und J. Zeitschr. f. Krystall. Bd. 40. (1905). 78—85.

the isomorphous substitution of the halogens *Cl*, *Br* and *I* in organic molecules. The author first gives a short résumé of the chief series of inorganic compounds where *Cl*-, *Br*- and *I*-compounds have been compared in regard to their crystal-form. Even in cases where a direct analogy in form does *not* occur an isodimorphism may be always proved to exist.

The *I*-compounds differ in most cases from the others as regards their behaviour.

Only a few complete series of analogous halogen derivatives of organic compounds have been investigated and in no case as to their mutual behaviour in the liquid state.

A complete crystallographical investigation was made of: *p*-Chloro-, *p*-Bromo- and *p*-Iodoacetanilide ¹⁾, the melting points of which are respectively, 179°, 167½° and 181°. The *Bromo*- and the *Iodo*-compounds are both *monoclinic*, the *Chloro*-compound differs and is *rhombic*. The *Br*- and the *I*-compound present in symmetry and parameters a distinct analogy with the *rhombic Cl*-compound; the plane of cleavage is, however, a totally different one ²⁾.

Cl-compound: Rhombo-pyramidal.

$a : b : c = 1,3347 : 1 : 0,6857$; $\beta = 90^{\circ}0'$. Cleavable towards {100}.

Br-compound: monoclinoprismatic ³⁾

$a : b : c = 1,3895 : 1 : 0,7221$; $\beta = 90^{\circ}19'$. Cleavable towards {301}.

I-compound: monoclinoprismatic. ⁴⁾

$a : b : c = 1,4185 : 1 : 0,7415$; $\beta = 90^{\circ}29'$. Cleavable towards {301}.

GOSSNER ⁵⁾ proved that the *Cl*-compound is *dimorphous* and also that it possesses a *more labile monoclinic* form. On the other hand, the *Br*- and *I*-compounds are certainly also *dimorphous* but here the *rhombic* modification is the *more labile*. The more labile and the more stable modifications possess very analogous parameters, although their molecular structures are different. He thinks however that the *irregular positions of the melting points* may be satisfactorily explained from all this.

On the other hand, in the series *Chlorobromo*-, *Dibromo*- and *Iodobromonitrophenol*, all three derivatives are directly-isomorphous with each other. (Structure: $(OH) : (NO_2) : Br = 1 : 2 : 4$; *Cl*, *Br* and *I* on 6).

¹⁾ B. GOSSNER, Z. f. Kryst. **38**. 156—158. (1904).

²⁾ FELS, Z. f. Kryst. **32**. 386 (1900); Idem **32**. 406.

³⁾ MUGGE, Z. f. Kryst. **4**. 335; FELS, Z. f. Kryst. **37**. (1903). 469; WILSON, Z. f. Kryst. **36**. 86. Abstract; PANEbianco, Z. f. Kryst. **4**. 393.

⁴⁾ SANSONI, Z. f. Kryst. **18**. 102.

⁵⁾ GOSSNER, Z. f. Kryst. **38**. 156—158.

This is the first properly investigated series of halogen-substitution products in organic chemistry where *Cl*, *Br*, and *I* replace each other in a directly isomorphous manner.

Notwithstanding this complete isomorphism there occurs here a remarkable abnormality in the position of the melting points, just as in the case of the isodimorphous *p*-Halogen acetanilides. This abnormality *cannot*, therefore, be explained in the manner described above; in fact it is quite incomprehensible:

<i>Cl</i> -compound:	m. p. 112° C.	Spec. gr.	2,111	Mol. Vol.	118,7
<i>Br</i> -	„ m. p. 117½° C.	„ „	2,434	„ „	121,1
<i>I</i> -	„ m. p. 104° C.	„ „	2,645	„ „	129,03

In this case it is the *I*-compound which exhibits an abnormal melting point.

From all this it is evident that there is still something strange, as regards the mutual morphotropous relations of the halogens, at least, in the case of organic compounds. Some facts relating thereto will therefore be communicated in what follows.

I have, frequently, published papers on the *Methyl esters* of *p*-Chloro-, and *p*-Bromobenzoic acid¹⁾. The *Chloro*- and *Bromo*-derivative each appeared to possess a different form, whereas the melting point line of binary mixtures should lead to the conclusion that an isodimorphism was present here, with a melting point line of the rising type, although it seemed impossible then to define by physico-chemical methods the *limits* of mixing for the two kinds of mixed crystals.

In order to treat the existing problem as fully as possible, I prepared first of all the corresponding *Fluoro*- and *Iodo*-compound.

p-Fluorotoluene kindly presented to me by Prof. HOLLEMAN was oxidised with KMnO_4 in alkaline solution, the *p*-Fluorobenzoic acid was separated with HCl and then esterified by means of methyl alcohol and hydrogen chloride. The ester, which has a strong odour of aniseseed oil, is a liquid rendering measurements impossible, but on the other hand the acid could be measured crystallographically.

p-Toluidine was diazotised and converted by means of KI into *p*-Iodotoluene, this was distilled with steam, recrystallised and oxidised as directed to *p*-Jodobenzoic acid. In the same manner, *p*-Aminobenzoic acid was converted by diazotation etc. into its acid and this was

¹⁾ JAEGER, Neues Jahrb. f. Miner. Geol. und Palaeont. (1903). Beil. Bd. 1—28; Zeits. f. Kryst. 38. (1903). 279—301.

purified by sublimation. Both *Iodobenzoic acids* thus obtained were then esterified by means of methyl alcohol and HCl.

The product so obtained was purified by repeated recrystallisation from boiling alcohol until the melting point became constant at 114° .

The methyl ester of *p-Iodobenzoic acid* m.p. 114° crystallises from ether + alcohol in colourless needles, having a faint odour of aniseseed oil, which are very neatly formed, and exhibit the form of fig. 8.

Rhombo-bipyramidal.

$$a : b : c = 1,4144 : 1 : 0,8187.$$

Forms observed; $a = \{100\}$, predominant, very strongly lustrous, sometimes with delicate, vertical stripes; $p = \{210\}$, very sharply reflecting; $b = \{110\}$, narrow, often absent, but yields very sharp reflexes; $v = \{122\}$ and $r = \{011\}$, well-developed; $o = \{112\}$, very small and often absent altogether.

Habit: flattened towards $\{100\}$, with tendency parallel to the c -axis.

Angular measurements:

	Measured:	Calculated:
$a : p = (100) : (210) =$	$35^{\circ}15\frac{3}{4}'$	—
$b : v = (010) : (\bar{1}22) =$	$51^{\circ}49'$	—
$b : p = (010) : (210) =$	$54^{\circ}44\frac{1}{2}'$	
$v : v = (122) : (\bar{1}22) =$	$76^{\circ}23'$	$76^{\circ}22'$
$b : r = (010) : (011) =$	$50^{\circ}24\frac{1}{2}'$	$50^{\circ}41\frac{1}{2}'$
$a : v = (100) : (122) =$	$77^{\circ}29'$	$77^{\circ}23'$
$v : v = (122) : (\bar{1}22) =$	$25^{\circ}42'$	$25^{\circ}41'$
$r : r = (011) : (0\bar{1}1) =$	$79^{\circ}12'$	$79^{\circ}11'$
$v : r = (122) : (011) =$	$12^{\circ}50\frac{1}{2}'$	$12^{\circ}37'$
$p : r = (210) : (011) =$	$68^{\circ}23'$	$68^{\circ}33'$
$v : o = (122) : (112) =$	$17^{\circ}0\frac{1}{2}'$	$16^{\circ}43\frac{1}{2}'$
$o : o = (112) : (\bar{1}\bar{1}2) =$	$43^{\circ}3'$	$42^{\circ}55\frac{1}{2}'$

Cleavable towards $\{010\}$.

The optical axial plane is $\{001\}$ with the b -axis as first bisectrix. The apparent axial angle in α -monobromonaphthalene is about 80° ; the dispersion is $\rho < v$. On a , p and b orientated extinction.

The sp. gr. of the crystals is: 2,020 at 10° ; the equivalent volume = 129,7.

Topic axes $\chi : \psi : \omega = 6,8179 : 4,8203 : 3,9464$.

From the above it follows that the *I*-compound is *perfectly isomorphous* with the analogous *Br*-compound. By way of comparison

some of the chief data observed in both compounds are placed here in juxtaposition :

<i>p</i> -Iodobenzoic Ester :	<i>p</i> -Bromobenzoic Ester :
Rhombo-bipyramidal	Rhombo-bipyramidal
$a : b : c = 1,4144 : 1 : 0,8187$	$a : b : c = 1,3967 : 1 : 0,8402$
Forms :	Forms :
{100}, {010}, {011}, {210}, {112}, {122}.	{100}, {010}, {011}, {210}, {112}, {122}
On {100} delicate stripes parallel <i>c</i> -axis.	On {100} delicate stripes parallel <i>c</i> -axis.
Cleavable along <i>b</i> .	Imperfectly cleavable along <i>b</i> .
Axial plane is {001}; 1 st Diag. is <i>b</i> .	Axial plane is {010}; 1 st Diag. is <i>b</i> .
Angles:	Angles:
$a : p = 35^{\circ}16'$	$a : p = 34^{\circ}56'$
$b : v = 51^{\circ}49'$	$b : v = 51^{\circ}10'$
$o : o = 42^{\circ}55$ etc.	$o : o = 43^{\circ}50'$ etc.

The dispersion in the *I*-derivative is of an opposite character to that in the *Br*-compound; the apparent axial angles are almost equal if that of the *I*-derivative is measured in α -Bromonaphthalene and that of the *Br*-derivative in oil of Cassia.

It seems remarkable, that in our case the *Bromo*- and *Iodo*-compounds behave in an analogous manner and that it is the *Chloro*-compound which exhibits here a *deviating* character.

In order to show the further relation of the three compounds the binary melting point lines were determined and represented in fig. 9.

The melting point line *Br-I*-compound does not deviate markedly from the straight line, the difference is really negligible. The lowering of the melting point of the *I*-derivate is, therefore, practically directly proportional to the number of added molecules of the *Br*-compound.

The melting point lines *Cl-I*- and *Cl-Br*-compound take an analogous course, that is to say, all the melting points lie between the lowest and the highest melting point. Both melting point lines belong to the *rising* type of ROOZEBOOM, which may occur in isodimorphous substances. The lower branch and the mixing limits could not be found by thermometrical methods. The existence of these two branches may indeed be proved, and they are even situated at some considerable distance from the top branches — at least at the side of the compounds having the highest melting points — as was found by Dr. B. R. DE BRUYN. It is, however, not possible to determine this line with sufficient accuracy. The progressive change of the cooling-curve is of such a nature that a discontinuity is observed from which we

may draw the above mentioned conclusion that the lower branch of the melting point line — at least at the side of the *rhombic* mixed crystals — is situated at a fairly considerable distance from the upper

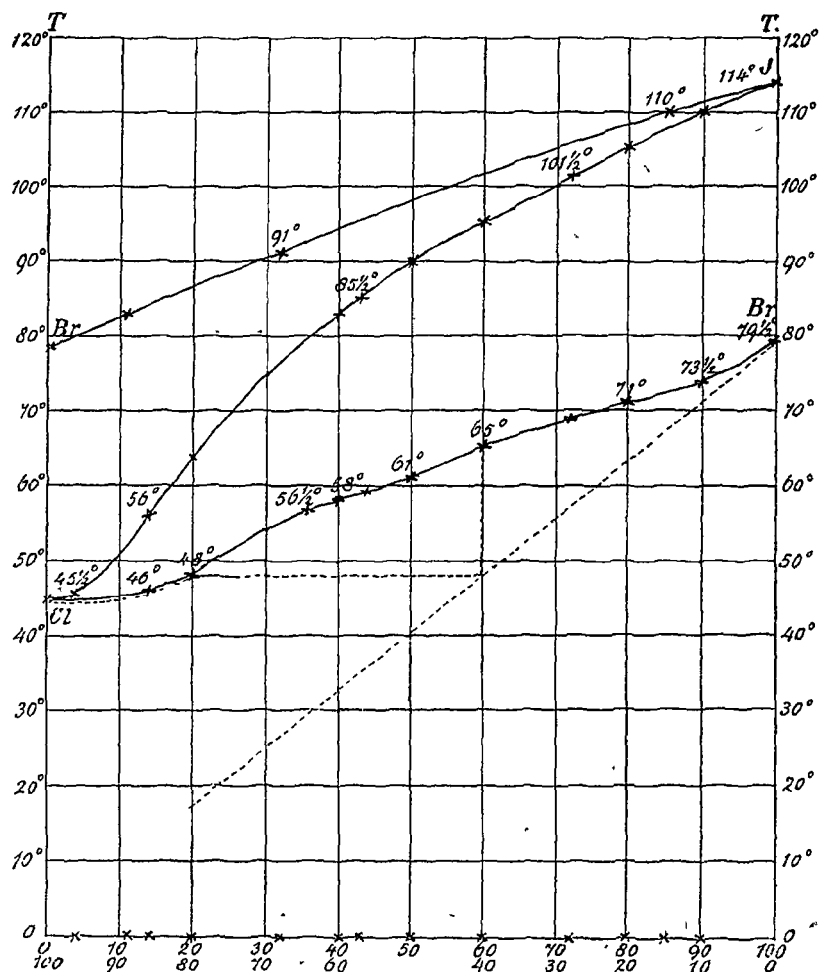


Fig. 9. Binary melting point lines of the three halogenised benzoic methyl esters.

branch. This change in direction of the cooling line is, however, so slight, that the true situation of the point on the lower branch cannot be indicated with certainty.

The determination of the mixing limits by an investigation of the solid phases, which are in equilibrium with solutions of known content, met with difficulties of an analytical character. An effort was, therefore, made to determine those mixing limits by the crystallographic process. For that purpose solutions were prepared of mixtures of the two esters, for instance of the *chloro*- and the *bromo*-ester,

in ether + alcohol, and the homogeneous mixed crystals obtained on slow evaporation were individually investigated crystallographically and then their melting point was taken, namely the temperature at which the last particle of solid matter disappears in the surrounding fused mass. If one may assume that this last solid particle, in each of the cases investigated, is really in *stable* equilibrium in regard to the fused mass, the temperature thus found, by comparison with the already found upper branch, indicates the molecule-percentage composition of the mixed crystal under investigation.

If we take little of the *Br*-ester and much of the *Cl*-ester, we obtain from the alcoholic solution *monoclinic* mixed crystals which possess quite the form and angular values of monoclinic *Cl*-ester itself. Of such crystals the melting point never exceeded $46\frac{1}{2}^{\circ}$. If the proportion of the components is reversed mixed crystals of a rhombic form are deposited quite analogous to the *Br*-ester. These crystals gave melting points from $79\frac{1}{2}^{\circ}$ down to 47° ; but not lower.

Assuming that the melting point of the end terms of the monoclinic series does not differ practically from 47° , it then looks as if rhombic mixed phases may exist which, at 47° as transition temperature, attach themselves *immediately* to the monoclinic terms. I have found, however, that rhombic mixed crystals with various melting points kept together in a closed tube for four months become turbid and partially opaque with a rough surface as soon as their melting point falls *below* 65° . It is also remarkable that the rhombic mixed phases of this kind are more and more badly formed and curve-planed, and that they become more distorted, as if existing in a kind of enforced condition, when their composition begins to differ from that at 65° towards the monoclinic side. It seems to me that when accepting the above hypothesis, all rhombic mixed phases below 65° represent *metastable* conditions, which, in the solid state, are very slowly broken up, to be partly converted into monoclinic terms.

That is to say the melting figure takes schematically the form of fig. 9; the said metastable conditions are then points situated on the extended part of the lower branch to the right, which indicates the composition of the rhombic mixed crystals coexisting with the fused mass. The stable hiatus in the mixing series then extends from 18% to 60% of the *Br*-compound.

From all this it follows that in consequence of the *very slow* conversion of the mixed crystals, no sharp determination of the mixing limits can be made in this manner when less than 60% *Br*-ester of monoclinic character is present.

In the system *Cl*-ester + *I*-ester the matter is still more troublesome.

There, the end term of the monoclinic mixing series is situated still much closer to the axis than in the case mentioned. In consequence of the very great difference in solubility of the *Cl*-, and the *I*-compound we never obtain here from alcoholic solutions anything else but *rhombic* very delicate needles, while the monoclinic phases crystallise so indistinctly that they are quite unsuitable for a serious investigation.

The *Br*-, and the *I*-ester readily crystallise together in *all* proportions with angular values which differ but little from those of the components. No optical anomalies could be found in such mixed phases. From this it follows that to those two halogen substitution products belongs an analogous molecular structure. Their molecular volumes in the solid condition agree indeed very well; the difference is smaller than between that of the *Cl*-, and *Br*-compounds.

As regards the lowering of the melting point of the compound melting at the higher temperature by addition of the one melting at the lower temperature, this is not proportionate to the number of added molecules, as in the system *Br* + *I*-compound. In the mixtures of *Cl*- and *I*-ester, the observed values are always situated on a curve which occurs *above* the line of the proportionate lowering of the melting point; in the system *Cl*- and *Br*-ester, on a two-periodic curve which occurs *below* the said straight line.

It must also be observed that the mixed phases deposited from alcoholic solutions possess a larger content in the compound melting at the higher temperature than the solution from which they have formed. For instance, from a solution containing 20 % of *Br*-ester and 80 % of *Cl*-ester, mixed (*rhombic*) crystals were at first deposited which melted at 57° corresponding with a considerably higher percentage of the *Br*-compound.

The *Chloro*-compound which is *monoclinic* with:

$$a : b : c = 1,8626 : 1 : 3,4260, \text{ and } \beta = 64^{\circ}18'$$

and the forms:

$a=\{100\}$, $c=\{001\}$, $r=\{\bar{1}02\}$, $p=\{210\}$, $t=\{011\}$, $o=\{\bar{1}11\}$, $s=\{111\}$, $w=\{\bar{1}13\}$. presents a habit which is not at all like that of the two other derivatives, although that habit, as shown in fig. 1—5, is in a high degree variable, according to the choice of the solvent and temperature of crystallisation.

The habit of the *Br*- and *I*-compound is on the other hand perfectly analogous; in the *I*-ester it is, moreover, very constant under different conditions of crystallisation (fig. 8) whilst it is still some-

what changeable in the *Br*-ester (fig. 6 and 7), although no longer so strong as in the *Cl*-derivative. With an increasing atomic weight of the halogens, the changeability of the crystal-habit, owing to a change in conditions of crystallisation, decreases considerably and gradually.

The sp. gr. of the three compounds, their equivalent volume and their topic parameters are :

Cl-ester: $d_{20} = 1,382$; $V = 123,37$. $\chi : \psi : \omega = 5,1731 : 2,7774 : 9,5153$.

Br-ester: $d_{20} = 1,689$; $V = 127,29$. $\chi : \psi : \omega = 6,6611 : 4,7691 : 4,0070$.

I-ester: $d_{20} = 2,020$; $V = 129,70$. $\chi : \psi : \omega = 6,8179 : 4,8203 : 3,9464$.

It must be remarked here that the melting points of the three esters increase *regularly* by $35\frac{1}{2}^{\circ}$ *notwithstanding* the difference in crystalform : $44^{\circ} - 79\frac{1}{2}^{\circ} - 114^{\circ}$.

The above admits of no other explanation than the assumption that all three halogenised esters are dimorphous. The *Cl*-ester must still exist in a *more labile rhombic* form and the *Br*- and *I*-esters in a *more labile monoclinic* form. In one of BRUNI's communications¹⁾ a "monoclinic" *p*-Bromobenzoic Methyl Ester is described by an Italian investigator with the object of proving an "isomorphism" with the analogous *p*-Nitrobenzoic ester. The given measurements have, however, absolutely no connection with those applied to the *p*-Chlorobenzoate, so that this monoclinic form can in no case be the one intended. Moreover, none of the measured angular values of the *p*-Bromo-derivative agree with those obtained by myself. It appears to me doubtful whether the measurements mentioned in BRUNI's paper are really correct or it may be that the operator has really not been working with *p*-Bromobenzoic Methyl ester at all. All efforts made by me to obtain from this substance a crystal form different to the *rhombic one* proved fruitless, whilst in the Italian treatise, the supposed "monoclinic" form is represented as a perfectly stable one which, therefore, occurs continuously.

In order to prove an eventually existing dimorphism of these substances, I have made use of LEHMANN's microscopical method with the aid of the crystallisation microscope constructed by him. It appeared, however, that in none of these cases a positive result could be obtained. I think that in the case of each of these substances, I can notice two different ways of crystallisation under the microscope, namely long, rather delicate needles and also parallelogram-limited

¹⁾ BRUNI and PADOA, Gazz. Chimic. Ital. (1904). 34a. 133—143; Rendic. Lincei (1903). 5a. 12. 348.

flat needles which exhibit higher interference colours and like the first named extinguish normally on the longitudinal direction. However, the difference — if present at all — is so indistinct that taking into consideration the inclination of these substances to alter their crystal-habitus under various circumstances in so high a degree, I dare not conclude to an already proved dimorphism. Experiments with mixtures richer or poorer in *Chloro*-ester also exhibited the same properties. It is, therefore, quite possible that we have two forms for each of the three substances, but this has not yet been *proved* and also it could not be ascertained whether in the given circumstances both eventually present forms stood to each other in the position of monotropy or enantiotropy.

A few short data as to the halogenised benzoic acids deserve mention.

1. *p*-*Chlorobenzoic acid* m.p. 243° has been measured by FELS (Zeitschr. f. Kryst. **32**, (1900) 389). It is monoclinic-prismatic, with $a : b : c = 1,2738 : 1 : 3,3397$, and $\beta = 78^{\circ}24\frac{1}{2}'$. The forms observed have intricate symbols; besides $a = \{100\}$ and $c = \{001\}$, he finds $d = \{207\}$, $o = \{111\}$, $e = \{233\}$, $u = \{322\}$, $v = \{411\}$. Sp.gr. = 1,541.

2. *p*-*Fluorobenzoic acid* m.p. 182° synthesised by me is also monoclinic-prismatic. If to the forms occurring here we assign the symbols: $a = \{100\}$, $c = \{001\}$, $r = \{203\}$, $s = \{403\}$, and $q = \{043\}$, the indices being therefore analogous to those given above, the parameters become :

$$a : b : c = 1,1917 : 1 : 3,1825$$

$$\beta = 78^{\circ}16'.$$

Although there exists here an undeniable difference in habit, I think I may still conclude that there is a direct isomorphism of the *Chloro*- and *Fluoro*-compound. A distinct plane of cleavage was not found. The melting point of *p*-*Fluorobenzoic acid* is also elevated by addition of the *Cl*-compound.

Angular values:

$$c' : r = 69^{\circ}56'$$

$$r : s = 15^{\circ}36'$$

$$s : a = 16^{\circ}14'$$

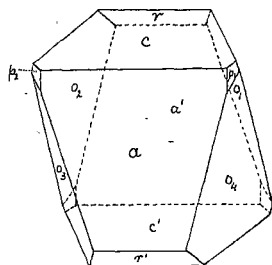
$$c : a = 78^{\circ}16'$$

$$c : q = 76^{\circ}28'$$

$$q_1 : q_1 = 27^{\circ}4'$$

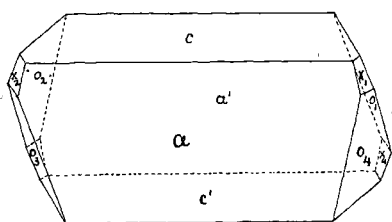
The habit is thin-tabled towards *c*, with a rectangular circumference. The crystals were obtained from alcohol + ether and were generally badly formed. The extinction on *c* is orientated.

Fig. 1.



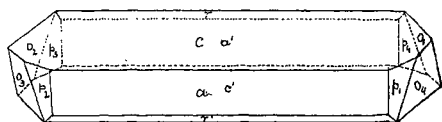
p-Chlorobenzoic Methyl ester.
From methyl alcohol, at a lower temperature.

Fig. 3.



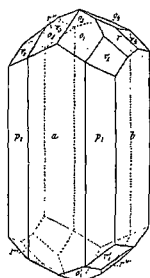
p-Chlorobenzoic Methyl ester.
From methyl alcohol, at a higher temperature.

Fig. 5.



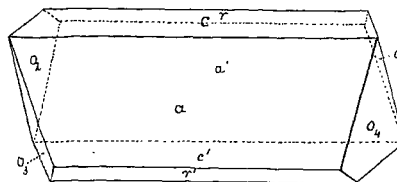
p-Chlorobenzoic Methyl ester.
From ether, at a lower temperature.

Fig. 7.



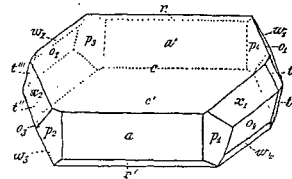
p-Bromobenzoic Methyl ester.
From ether.

Fig. 2.



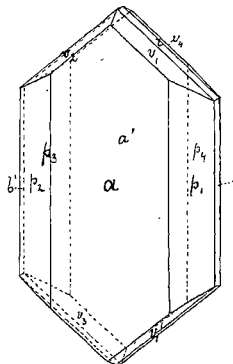
p-Chlorobenzoic Methyl ester
From methyl alcohol, at a higher temperature.

Fig. 4.



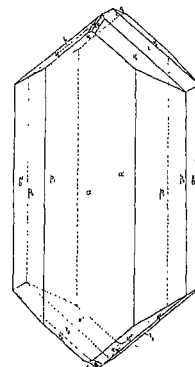
p-Chlorobenzoic Methyl ester.
From ethyl alcohol, at a higher temperature.

Fig. 6.



p-Bromobenzoic Methyl ester.
From methyl alcohol

Fig. 8.



p-Iodobenzoic Methyl ester.
From ethyl alcohol + ether.

3. *p*-Bromobenzoic acid, m.p. 252° was obtained by me in tiny crystals from ethyl acetate + benzene but they were very badly formed. They are monoclinic and probably quite isomorphous with the two other acids. The angle of inclination amounts to about 78½°.

4. *p*-Iodobenzoic acid has not as yet been obtained in measurable crystals owing to its little solubility in most of the organic solvents. Its melting point is situated at 267°, therefore higher than that of the *Br*-derivative. A direct isomorphism with the three other halogen benzoic acids is not improbable.

Physiology. — “*On catalases of the blood*”. By L. VAN ITALLIE.
(Communicated by Prof. C. A. PEKELHARING.)

(Communicated in the meeting of December 30, 1905).

The discovery made by THÉNARD that bloodfibrine possesses the property of decomposing hydrogenperoxide has also been extended to defibrinated blood, by SCHÖNBEIN (*Journ. f. prakt. Chemie* **89**, 22). It has found a practical application in the judicial investigation on bloodtraces and has been the object of manifold scientific investigations. A resuming report precedes the investigations by SENTER (*Das Wasserstoffsuperoxyd zersetzende Enzym des Blutes. Zeitschr. f. physik. Chemie* **44** [1903] 257—318) to whose work we refer the reader. SENTER calls the enzyme which he has isolated from blood *Haemase* whereas I myself prefer to use the name of *catalase*, which has been given by LOEW (*Catalase, A new enzym of general occurrence, Report N°. 68 U. S. Depart. of Agriculture. Washington*).

Although the catalases, those enzymes which are able to split H₂O₂ in water and oxygen, are universally scattered in the vegetable and animal kingdom, it has as yet not been possible to isolate one of these bodies in state of purity.

Although different phenomena indicate that there exist more than one catalase (apart from LOEW's α - and β -varieties) it has been impossible as yet to discern them.

The following communication gives a new contribution to the properties of the catalases of the blood, which may perhaps lead to a differentiation of the catalases, and which at least gives an opportunity of dividing the catalases of some animals into two groups.

To Mr. C. J. KONING at Bussum I owe the communication that human-blood diluted from 1—1000 heated at 63° for half an hour,