

Citation:

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Crystallography. — “On a new case of form-analogy and miscibility of position-isomeric benzene-derivatives, and on the crystal-forms of the six Nitrodibromobenzenes.” By Dr. F. M. JAEGER.
(Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of April 27, 1906).

§ 1. The following contains the investigation of the crystal-forms exhibited by the six position-isomeric *Nitrodibromobenzenes*, which may be expected from the usual structure-representations of benzene. It has been shown that, in this fully investigated series, there again exists a miscibility and a form-analogy between two of the six terms.

The above compounds were kindly presented to me by Prof. HOLLEMAN, to whom I again express my thanks.

This investigation is connected with that on the isomeric *Dichloronitrobenzenes*, which has also appeared in these proceedings (1905, p. 668).

A. Nitro-2-3-Dibromobenzene.

Structure: $C_6H_3 \cdot (NO_2) \cdot Br \cdot Br$; meltingpoint: $53^\circ C$.
(1) (2) (3)

The compound, which is very soluble in most organic solvents,

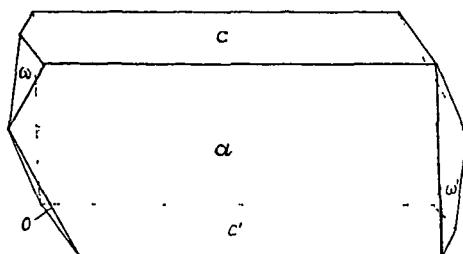


Fig. 1.

crystallises best from ligroin + ether in small, flat, pale sherry-coloured needles which generally possess very rudimentary terminating planes.

Triclinic-pinacoidal.

$$a : b : c = 1,4778 : 1 : 1,9513.$$

$$A = 90^\circ 30'$$

$$B = 110^\circ 37'$$

$$C = 90^\circ 16\frac{1}{2}'$$

$$\alpha = 90^\circ 45\frac{2}{3}'$$

$$\beta = 110^\circ 36\frac{3}{4}'$$

$$\gamma = 89^\circ 59\frac{1}{4}'$$

The crystals, therefore, show a decided approach to the monoclinic system; on account, however, of their optical orientation, they can only be credited with a triclinic symmetry.

The forms observed are: $a = \{100\}$, strongly predominant and very lustrous; $b = \{010\}$, smaller but yielding good reflexes; $c = \{001\}$, narrower than a , but very lustrous; $o = \{1\bar{1}\bar{1}\}$, well developed and very lustrous; $\omega = \{1\bar{1}\bar{1}\}$, smaller but very distinct; $s = \{1\bar{1}\bar{1}\}$, very narrow but readily measurable.

The habit is elongated towards the b -axis with flattening towards $\{100\}$.

	<i>Measured :</i>	<i>Calculated :</i>
$a : b = (100) : (0\bar{1}0) =$	$90^{\circ}16\frac{1}{2}'$	—
$a : c = (100) : (001) =$	$69\ 23$	—
$a : o = (100) : (1\bar{1}\bar{1}) =$	$65\ 11$	
$c : o = (00\bar{1}) : (1\bar{1}\bar{1}) =$	$75\ 47\frac{1}{3}$	—
$b : o = (0\bar{1}0) : (1\bar{1}\bar{1}) =$	$36\ 6$	—
$a : \omega = (100) : (1\bar{1}\bar{1}) =$	$50\ 52$	$50^{\circ}49'$
$c : \omega = (001) : (1\bar{1}\bar{1}) =$	$56\ 52$	$56\ 43$
$b : \omega = (0\bar{1}0) : (1\bar{1}\bar{1}) =$	$46\ 28$	$46\ 35$
$o : \omega = (1\bar{1}\bar{1}) : (1\bar{1}\bar{1}) =$	$47\ 13$	$47\ 29\frac{2}{3}$
$a : s = (\bar{1}00) : (\bar{1}\bar{1}\bar{1}) =$	$49\ 59$	$50\ 49\frac{1}{3}$
$b : s = (0\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	$45\ 48$	$45\ 52\frac{1}{3}$
$c : s = (00\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	—	$56\ 4$
$o : s = (1\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	$63\ 39$	$63\ 59\frac{2}{3}$

Readily cleavable, parallel $\{100\}$.

The extinction on $\{100\}$ amounts to about $26\frac{1}{2}$ in regard to the b -axis; in convergent light a hyperbole is visible occupying an eccentric position.

The sp. gr. of the crystals is 2,305 at 8° ; the equivalent volume 121.47.

B. Nitro-2-5-Dibromo-Benzene.

Structure: $C_6H_3 \cdot (NO_2)_{(1)} \cdot Br_{(2)} \cdot Br_{(3)}$; m.p.: $84^{\circ}, 5$.

This compound has been previously studied crystallographically by G. FRIE, (Zeits. f. Kryst. **32**, 377). This paper, however, contains several errors, which render a renewed investigation desirable; moreover, another choice of axial (coordinate) planes is required, which makes the crystals show more analogy with the other triclinic terms of this series.

The crystals deposited from acetone + ligroin have the form of small plates flattened towards $\{001\}$ (figs. 2 and 3). They are pale yellow and very lustrous.

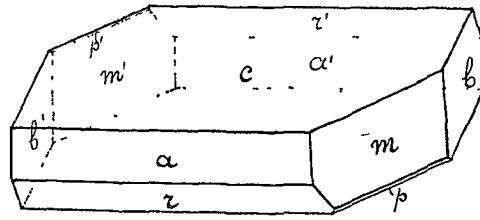


Fig. 2.

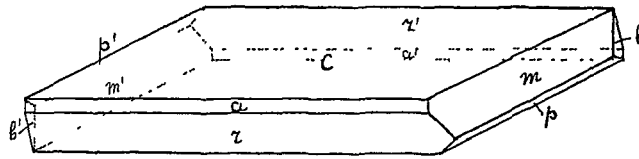


Fig. 3.

Triclinio-pinacoïdal.

$$a : b : c = 1,4909 : 1 : 2,0214.$$

$$A = 91^{\circ} 3\frac{1}{2}' \quad a = 90^{\circ} 57\frac{1}{2}'$$

$$B = 113^{\circ} 21\frac{1}{2}' \quad \beta = 113^{\circ} 21\frac{1}{3}'$$

$$C = 90^{\circ} 27' \quad \gamma = 90^{\circ} 2'.$$

Forms observed: $c = \{001\}$, strongly predominant and reflecting ideally; $a = \{100\}$, and $r = \{\bar{1}01\}$, usually developed equally broad and also yielding sharp reflexes; $b = \{010\}$, smaller, readily measurable; $m = \{110\}$, large and lustrous; $p = \{11\bar{3}\}$, mostly narrow but very lustrous; sometimes as broad as m .

Broad flattened towards $\{001\}$. The approach to monoclinic symmetry is also plain in this case.

	<i>Measured:</i>	<i>Calculated:</i>
$a : b = (100) : (010) =$	$*89^{\circ} 33'$	—
$b : c = (010) : (001) =$	$*88 \ 56\frac{1}{2}'$	—
$c : a = (001) : (100) =$	$*66 \ 38\frac{1}{2}'$	—
$b : m = (010) : (110) =$	$*35 \ 59\frac{1}{2}'$	—
$a : r = (100) : (10\bar{1}) =$	$*43 \ 45$	—
$c : m = (001) : (110) =$	$75 \ 46$	$75^{\circ} 38\frac{2}{3}'$
$a : m = (100) : (110) =$	$53 \ 33$	$53 \ 33\frac{1}{2}'$
$c : r = (00\bar{1}) : (10\bar{1}) =$	$69 \ 37$	$69 \ 36\frac{1}{2}'$
$r : m = (10\bar{1}) : (110) =$	$65 \ 20$	$65 \ 11$
$p : m = (11\bar{3}) : (110) =$	$60 \ 59$	$60 \ 44\frac{1}{2}'$
$r : b = (10\bar{1}) : (010) =$	$89 \ 55$	$89 \ 22$
$r : p = (10\bar{1}) : (11\bar{3}) =$	$50 \ 53$	—

Readily cleavable, parallel m .

The optical orientation is that of FELS, in which his forms {010}, {001} and {11 $\bar{1}$ } assume, respectively, in my project the symbols {001}, {110} and {010}. It may be remarked that FELS has incorrectly stated the structure and also the melting point. Moreover, his angles (11 $\bar{1}$):(100) and (11 $\bar{1}$):(010) appear to be $> 90^\circ$. Perhaps it is owing to this, that the agreement between the calculated and found values is with him so much more unfavourable than with me. I have never observed forms { $\bar{5}52$ } and { $\bar{1}5.15.4$ }

The sp. gr. at 8° is 2,368; the equiv. volume: 118,66.

Topical axes: $\chi : \psi : \omega = 5,2190 : 3,5005 : 7,0758$.

On comparing the said position-isomeric derivatives, one notices at once not the great similarity between the two compounds, which, although constituting a case of direct-isomorphism, still very closely resembles it.

Nitro-2-3-Dibromobenzene.

Triclino-pinacoidal.

$a : b : c = 1,4778 : 1 : 1,9513$

$A=90^\circ 30' B=110^\circ 37' C=90^\circ 16\frac{1}{2}'$

$\alpha=90^\circ 45\frac{2}{3}' \beta=110^\circ 36\frac{3}{4}' \gamma=89^\circ 59\frac{1}{4}'$

$\chi : \psi : \omega = 5,2565 : 3,5571 : 6,9409$.

However:

Forms: {100}, {010}, {001}, {1 $\bar{1}\bar{1}$ },
{ $\bar{1}\bar{1}1$ } and { $\bar{1}\bar{1}\bar{1}$ }

Cleavable parallel {100}.

Habit tabular towards {100}.

Nitro-2-5-Dibromobenzene.

Triclino-pinacoidal.

$a : b : c = 1,4909 : 1 : 2,0214$.

$A=91^\circ 3\frac{1}{2}' B=113^\circ 21\frac{1}{2}' C=90^\circ 27'$

$\alpha=90^\circ 57\frac{1}{2}' \beta=113^\circ 21\frac{1}{3}' \gamma=90^\circ 2'$

$\chi : \psi : \omega = 5,2190 : 3,5005 : 7,0758$.

However:

Forms: {100}, {010}, {001}, { $\bar{1}01$ },
{110}, {11 $\bar{3}$ }.

Cleavable parallel {110}.

Habit tabular towards {001}.

We, therefore, still notice such a difference in habit and cleavability that a direct isomorphism, in the ordinary meaning of the word; cannot be supposed to be present. There occurs here a case of isomorphotropism bordering on isomorphism.

Notwithstanding that difference, both substances can form an interrupted series of mixed crystals, as has been proved by the determination of the binary melting point curve and also crystallographically¹⁾.

The melting point of the 1-2-3-derivative (53°) is depressed by addition of the 1-2-5-derivative. The melting point line has also

¹⁾ The binary melting-curve possesses, — as proved by means of more exact determination, — a *eutectic point* of 52° C. at 2% of the higher melting component; therefore here the already published melting-diagram is eliminated. There is a *hiatus* in the series of mixed-crystals, from $\pm \frac{1}{2}\%$ to circa 48% of the 1-2-3-derivative. I shall, however point out, that the possibility of such a hiatus thermodynamically can be proved, — even in the case of directly-isomorphous substances.

(Added in the English translation).

not, as in the previously detected case of the two tribromotoluenes (Dissertation, Leyden 1903) a *continuous* form; the difference is caused by the lesser degree of form-analogy which these substances possess in proportion to that of the two said *tribromotoluenes*.

The third example of miscibility, — although partially —, and of form-analogy of position-isomeric benzene-derivatives¹⁾ is particularly interesting.

Mixed crystals were obtained by me from solutions of both components in acetone + ether.

They possess the form of fig. 1 and often exhibit the structure of a sand time-glass or they are formed of layers. With a larger quantity of the lower-melting derivative, long, delicate needles were obtained which are not readily measurable. The melting points lie between $\pm 75^\circ$ and $84\frac{1}{2}^\circ$; I will determine again more exactly the mixing limits.

C. Nitro-2-4-Dibromobenzene.

Structure: $C_6H_3 \cdot (NO_2)_{(1)} \cdot Br_{(2)} \cdot Br_{(4)}$; m. p. $61^\circ.6$.

Recrystallised from alcohol, the compound forms large crystals flattened towards *a* and elongated towards the *c*-axis. They are of a sulphur colour.

Triclino-pinacoidal.

$$a : b : c = 1,1307 : 1 : 1,1698.$$

$$\begin{array}{ll} A = 97^\circ 13\frac{1}{2}' & a = 97^\circ 36' \\ B = 113^\circ 30\frac{1}{2}' & \beta = 113^\circ 37' \\ C = 90^\circ 38\frac{1}{2}' & \gamma = 87^\circ 33' \end{array}$$

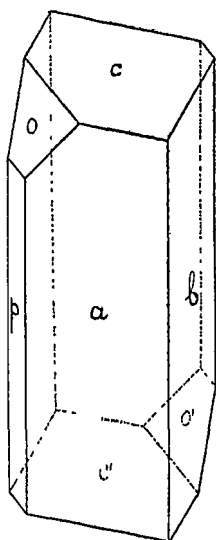


Fig. 4.

Forms observed: $a = \{100\}$ predominant and very lustrous; $b = \{010\}$ and $c = \{001\}$, equally broad, both strongly lustrous; $p = \{1\bar{1}0\}$, narrow but readily measurable; $o = \{1\bar{1}1\}$, large and yielding good reflexes.

The compound has been measured previously, by GROTH and BODEWIG (Berl. Berichte, **7**, 1563). My results agree in the main with theirs; in the symbols adopted here, their *a*- and *b*-axes have changed places and the agreement with the other derivatives of the series is more conspicuous.

¹⁾ The examples now known are 1-2-3-5-, and 1-2-4-6-*Tribromobenzene*; 1-2-3-5-*Tribromo-4-6-Dinitro-* and 1-2-4-6-*Tribromo-3-5-Dinitrotoluene*; and 1-2-5-, and 1-2-3-*Nitrodibromobenzene*, partially miscible.

	<i>Measured:</i>	<i>Calculated:</i>
$a : b = (100) : (010) =$	$* 89^{\circ} 21\frac{1}{2}'$	—
$a : c = (100) : (001) =$	$* 66 29\frac{1}{2}'$	—
$b : c = (010) : (001) =$	$* 82 46\frac{1}{2}'$	—
$p : a = (\bar{1}\bar{1}0) : (100) =$	$* 46 36$	—
$c : o = (001) : (\bar{1}\bar{1}1) =$	$* 48 42$	—
$o : p = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	$51 43$ (circa)	$52^{\circ} 1'$
$c : p = (001) : (\bar{1}\bar{1}0) =$	$100 29$ (circa)	$100 43'$

Cleavable towards $\{010\}$; GROTH and BODEWIG did not find a distinct plane of cleavage.

Spec. Gr. of the crystals = 2,356, at 8° C., the equiv. vol. = 119,27.

Topic Axes: $\chi : \psi : \omega = 5,2365 : 4,6304 : 5,4166$.

Although the analogy of this isomer with the two other triclinoisomers is plainly visible, the value of $a : b$ is here quite different. In accordance with this, the derivative melting at $84\frac{1}{2}^{\circ}$ lowers the melting point of this substance. A mixture of 87% 1-2-4- and 13% 1-2-5-Nitrodibromobenzene melted at 56° . There seems, however, to be no question of an isomorphotopous mixing.

D. Nitro-2-6-Dibromobenzene.

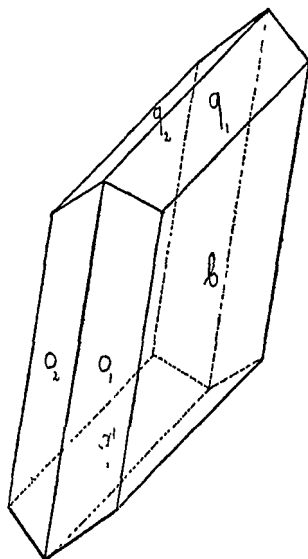


Fig. 5.

Structure: $C_6H_3(NO_2)_{(1)} \cdot Br_{(2)} \cdot Br_{(6)}$; m.p. 82° .

Recrystallised from alcohol the compound generally forms elongated, brittle needles which are often flattened towards two parallel planes.

Monoclinic-prismatic.

$$a : b : c = 0,5678 : 1 : 0,6257.$$

$$\beta = 83^{\circ} 24'.$$

Forms observed: $b = \{010\}$, strongly predominant; $q = \{011\}$ and $o = \{111\}$ about equally strongly developed. The crystals are mostly flattened towards b with inclination towards the a -axis.

	<i>Measured:</i>	<i>Calculated:</i>
$q : q = (011) : (0\bar{1}1) =^* 63^\circ 43\frac{1}{2}'$		—
$o : o = (111) : (1\bar{1}\bar{1}) =^* 47\ 52$		—
$o : q = (111) : (0\bar{1}1) =^* 74\ 20\frac{1}{2}'$		—
$o : q = (111) : (011) = 45\ 42\frac{1}{2}'$		45°42'
$q : b = (011) : (010) = 58\ 8\frac{1}{4}'$		58 8 $\frac{1}{4}$ '
$b : o = (010) : (111) = 66\ 6$		66 4

No distinct plane of cleavage is present. An optical investigation was quite impossible owing to the opaqueness of the crystals.

Sp. Gr. = 2,211 at 8° C.; the equiv. vol.: 127,09.

Topic parameters: $\chi : \psi : \omega = 4,0397 : 7,1147 : 4,4516$.

E. Nitro-3-5-Dibromobenzene.

Structure: $C_6H_3(NO_2)_{(1)} \cdot Br_{(3)} \cdot Br_{(5)}$; m.p.: 104°,5. The compound has already been measured by BODEWIG (Zeitschr. f. Kryst. 1. 590); my measurements quite agree with his.

Monoclinic-prismatic.

BODEWIG finds $a : b : c = 0,5795 : 1 : 0,2839$, with $\beta = 56^\circ 12'$. Forms: {110}, {100}, {001} and {011}.

I take $\beta = 85^\circ 26'$ and after exchanging the a -, and c -axis

$$a : b : c = 0,5678 : 1 : 0,4831,$$

with the forms {011}, {001}, {201} and {211}. Completely cleavable towards {201}. Strong, negative double refraction.

Sp. Gr. = 2,363 at 8° C.; equiv. vol. = 118,91.

Topic axes: $\chi : \psi : \omega = 4,3018 : 7,5761 : 3,6601$.

The great analogy in the relation $a : b$ of this and of the previous substance is remarkable; also that of the value of angle β .

F. Nitro-3-4-Dibromo-Benzene.

Structure $C_6H_3(NO_2)_{(1)} \cdot Br_{(3)} \cdot Br_{(4)}$; m.p. 58° C. Has been measured by GROTH and BODEWIG (Berl. Ber. 7.1563). *Monoclinic-prismatic.*

$a : b = 0,5773 : 1$ with $\beta = 78^\circ 31'$. Forms {001}, {110} and {100}, tabular crystals. Completely cleavable towards {100}, distinctly so towards {010}. The optical axial plane is {010}; on a both optical axes (80°) are visible. I found the sp. gr. at 8° C. to be 2,354. The equivalent volume is therefore 119,34.

I have tried to find a meltingpoint-line of the already described type in the monoclinic derivatives in which some degree of form-analogy is noticeable. However, in none of the three binary mixtures this was the case; the lower melting point was *lowered* on addition of the component melting at the higher temperature, without formation of mixed crystals. For instance:

A mixture of 82,3% 1-2-3- and 17,7% 1-3-5-*Nitrodibromo-benzene* melted at 48½° C.

A mixture of 76,5% 1-2-6- and 23,5% 1-3-5-*Nitrodibromo-benzene* at 68½° C.

A mixture of 90,5% 1-3-4- and 9,5% 1-2-6-*Nitrodibromo-benzene* at 54° C.

Moreover, no mixed crystals could be obtained from mixed solutions.

The slight form-analogy with the *Nitro-dichloro-benzenes*¹⁾ investigated by me some time ago is rather remarkable.

Nitro-2-3-Dichloro-Benzene (62° C. rhombic) and *Nitro-2-6-Dichloro-Benzene* (71° C. monoclinic) exhibit practically no form-analogy with the two *Dibromo*-compounds. There is also nothing in the *Dichloro*-derivatives corresponding with the isomorphotropic mixture of the 2-3- and 2-5-*Dibromo*-product. The sole derivatives of both series which might lead to the idea of a direct isomorphous substitution of two *Cl*- by two *Br*-atoms are the *Nitro-3-5-Dihalogen-Benzenes* (65° C. and 104,5 C.); the melting point of the *Dichloro*-derivative is indeed *elevated* by an addition of the *Dibromo*-derivative.

As a rule, the differences in the crystal-forms of the compounds of the brominated series are much less than those between the forms of the chlorinated derivatives — a fact closely connected with the much greater value which the molecular weight possesses in the *Nitro-Dibromo-Benzenes* than in the corresponding *Chloro*-derivatives.

Zaandam, April 1906.

Physiology. — “*On the nature of precipitin-reaction.*” By Prof. H. J. HAMBURGER and Prof. SVANTE ARRHENIUS (Stockholm).

(Communicated in the meeting of April 27, 1906).

One of the most remarkable facts discovered during the last years in the biological department, is most certainly the phenomenon that when alien substance is brought into the bloodvessels the individual reacts upon it with the forming of an antibody. By injecting a

¹⁾ These Proc. VII, p. 668.