

*Citation:*

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In oil of cloves as immersion liquid the situation of the elasticity directions on the planes of {010}, {021} and {001} orientated normally in regard of the  $\alpha$ -axis. The optical axial plane is {100}; the first diagonal stands perpendicularly on {010}. On the planes of {021} a brightly coloured interferential image is visible in convergent polarised light; extraordinarily strong dispersion of a rhombic character with  $\rho > v$  around the first bissectrix. In oil of cloves the apparent axial angle amounts to about  $49^\circ$  for the red and  $46^\circ$  for the green rays.

The oil caused on {021} little solution-figures, which had the form of isosceles trapezia; they agree with the indicated symmetry of the crystals.

The specific gravity is 1,278, at  $15^\circ$ , the equivalent-volume is 189,28, and the topical axes are:

$$\chi : \psi : \omega = 6,0875 : 7,1175 ; 4,3688$$

Although differing from NORDENSKJÖLD's *para*-derivative in symmetry, the analogy of the two isomers is still distinctly recognisable in the value of the relation  $b : c$ .

*o*-Nitrobenzyl-*para*-Toluidine:  $a : b : c = 1,000 : 1 : 0,6230$ .

*o*-Nitrobenzyl-*ortho*-Toluidine:  $a : b : c = 0.8552 : 1 : 0,6138$ .

The difference in position of the methyl- and amino-group with regard to each other therefore causes chiefly only a variation of the crystal parameters in one direction.

**Chemistry.** — “*On position-isomeric Dichloronitrobenzenes.*” By Dr. F. M. JAEGER. (Communicated by Prof. A. F. HOLLEMAN).

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

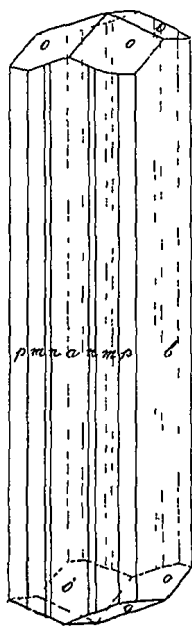
Of the six theoretically-possible dichloronitrobenzenes, which I received some time ago for investigation from Prof. HOLLEMAN, I succeeded in obtaining four in such a measurable form that their crystallographical determination could be satisfactorily undertaken.

Notwithstanding the great power of crystallisation of most of them, the preparation of properly developed crystals is a troublesome and very tedious matter. This is partly due to the very great solubility in most of the organic solvents, which in connection with the low melting points of these compounds often causes a not inconsiderable supersaturation. During the spontaneous crystallisation, which then takes place, no well-formed individuals, but crystal-aggregates are formed, which are difficult of investigation. In addition, the peculiar softness of the crystals causes most of them to exhibit curved planes and considerable geometrical deviations. Again, owing to the heat

of the source of light during the measurement the crystals soon become a dull surface, so that the inaccuracy of the measurements is still further increased by the less sharp limitation of the signal reflexes.

Of the substances examined the *ortho*-dichloroderivatives are both rhombic, the *meta*-derivatives probably all monoclinic and the *para*-dichloroderivative triclinic, only the geometrically well-defined substances of this series are described here in detail. In crystalline form they show comparatively little resemblance to each other, chiefly in consequence of the considerable deformation of the molecule owing to the mutual attraction of the Cl-atoms and of the (NO<sub>2</sub>)-group.

Fig. 1



1-2-Dichloro-3-Nitro-Benzene.

## a. 1-2-Dichloro-3-Nitro-Benzene.

C<sub>6</sub>H<sub>3</sub>. Cl. Cl. (NO<sub>2</sub>) ; melting point : 61° à 62° C.  
(1) (2) (3)

This compound crystallises from a mixture of ethyl-acetate and ether and also from glacial acetic acid, on very slow evaporation of the solvent, in colourless silky needles, which are limited by small, lustrous pyramidal planes (Fig. 1).

*Rhombic-bipyramidal.*

$$a : b : c = 0,6472 : 1 : 0,2780.$$

Forms observed :  $a = \{100\}$  and  $b = \{010\}$  equally strongly developed and both very lustrous ;  $p = \{230\}$ ,  $m = \{110\}$ ,  $n = \{430\}$ ; the latter form is the smallest of the three and reflects less sharply than  $p$  and  $m$ ;  $a$  sometimes shows a delicate streak parallel with  $o : a$ ;  $o = \{133\}$  lustrous, yielding good reflexes.

The vertical zone is, geometrically very well constructed. The angular values observed in different crystals differ but inconsiderably from the average values.

	<i>Measured:</i>	<i>Calculated:</i>
$a : p = (100) : (230) =$	*44° 9'	—
$o : o = (133) : (\bar{1}\bar{3}\bar{3}) =$	30 51½'	—
$p : m = (230) : (110) =$	11 21	11°14'
$m : n = (110) : (430) =$	7 7½'	7 1
$n : b = (430) : (010) =$	27 23	27 35½'
$a : o = (100) : (133) =$	82 16	82 7
$b : o = (010) : (103) =$	74 36	74 34
$o : o = (133) : (\bar{1}\bar{3}\bar{3}) =$	15 32	15 46

46\*

Readily cleavable along  $o$ . On  $m$  and  $p$  right-angled little etch-figures are visible in cassia-oil, which correspond with the indicated symmetry. In the vertical zone the direction of the optical elasticity axis is orientated on all the planes. An axial image was not observed.

The specific gravity of the needles as determined by means of a solution of mercuric-potassium-iodide was 1,721 at 14°. The equivalent-volume is therefore 111.56 and the topical axes become;

$$\chi : \psi : \omega = 5,5190 : 8,5272 : 2,3706..$$

b. 1-3-Dichloro-2-Nitro-Benzene.

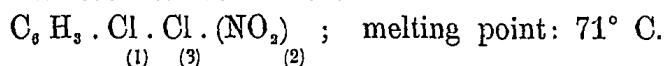
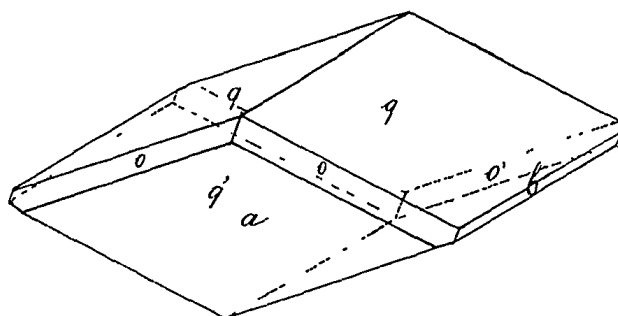
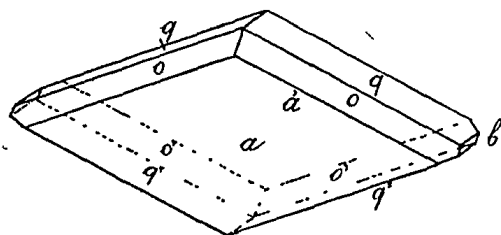


Fig. 2a



1-3-Dichloro-2-Nitro-Benzene.

Fig. 2b.



1-3-Dichloro-2-Nitro-Benzene.

reflecting;  $q = \{011\}$ , lustrous and either quite as narrow as  $o$  or else the broadest developed of all, so that the crystals appear short-prismatic towards the clino-axis;  $o = \{111\}$ , generally small, mostly streaked parallel with  $a : o$  and reflecting rather dullisly;  $b = \{010\}$ , very small and often only present in a rudimentary form.

The compound crystallises from carbon disulphide in large, colourless, thin plates of parallelogram shape or also in smaller thick crystals as shown in figs. 2a and 2b. The crystals are often opaque and difficult

to measure; sometimes, however, they are more lustrous and very clear.

*Monoclinic-prismatic.*

$$a : b : c = 0,6696 : 1 : 0,4149.$$

$$\beta = 87^\circ 51\frac{2}{3}'.$$

Forms observed:  $a = \{100\}$  generally strongly predominating and always sharply

*Measured:*      *Calculated:*

$a : o = (100) : (111) =$	$58^\circ 44'$	—
$q : q = (011) : (0\bar{1}1) =$	$45 \frac{2}{3}$	—
$a : q = (100) : (011) =$	$88 \frac{1}{2}$	—
$o : q = (111) : (01\bar{1}) =$	127 55	128°25'
$o : q = (111) : (011) =$	29 17	29 17½'
$a : b = (100) : (010) =$	89 57	90 0
$o : o = (111) : (1\bar{1}1) =$	38 38 (about)	38 16

A distinct cleavability was not observed.

The crystals deposited from acetone, which were very large but dull, show a predominance of  $a$  over  $b$ ; they are much elongated along the vertical axis and further possess a form which is probably {233} with  $(233) : (100) = 67^\circ 33'$ , calculated  $67^\circ 24'$ . On  $a$  there is diagonal extinction; the optical axial plane is {010}. One optical axis descends almost perpendicularly on  $a$ .

The specific gravity is 1,603, at  $17^\circ$ , the equivalent volume 119,77.

Topical axes:  $\gamma : \psi : \omega = 5,0596 : 7,5561 : 3,1350$ .

Although the parameter-relation  $a : b$  and the angle  $\beta$  in this isomer are comparable with those of the 1-2-3-derivative:

1-3-Dichloro-2-Nitro-Benzene:  $a : b = 0,6696 : 1$ ;  $\beta = 87^\circ 52'$

1-2-Dichloro-3-Nitro-Benzene:  $a : b = 0,6472 : 1$ ;  $\beta = 90^\circ$ .

their crystalline forms are still rather different; the relation  $\frac{b}{c}$  of the latter substance is about  $1\frac{1}{2}$ , that of the first derivative.

c. 1-3-Dichloro-5-Nitro-Benzene.

$C_6H_3 \cdot Cl^{(1)} \cdot Cl^{(3)} \cdot (NO_2)^{(5)}$ ; melting point:  $65^\circ C$ .

In alcohol or glacial acetic acid, in which solvents the compound exhibits a remarkably great crystallisation power, there are generally formed very long, flat columns of considerable thickness, or also right-angled or obtusely truncated pale-sherry coloured small thin plates. Owing to the great softness of the substance and its great plasticity, the crystals are in most cases so ill-formed and distorted that measurements become impossible. With very slow evaporation we sometimes get better formed crystals although they are very poor in planes. They have a peculiar odour resembling nitrobenzene.

*Monoclinic-prismatic.*

$a : b = 0,5940 : 1$ ;  $\beta = 58^\circ 43'$ .

Forms observed:  $a = \{100\}$ , broad and very lustrous;  $b = \{010\}$ , narrower and less lustrous; it is often absent altogether;  $m = \{110\}$ , narrow and  $c = \{001\}$ , small but very reflecting; the habitus is elongated along the  $c$ -axis and then flattened  $\{100\}$ .

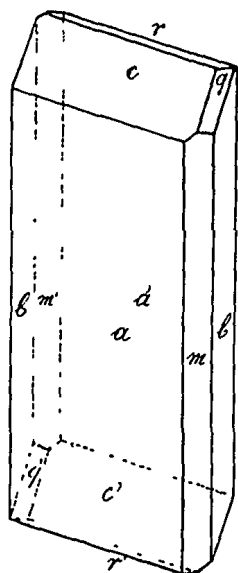
	<i>Measured:</i>	<i>Calculated:</i>
$b : m = (010) : (110) =$	* 63 5	
$a : c = (100) : (001) =$	* 58 43	—
$a : m = (100) : (110) =$	26 58	$26^\circ 55'$
$m : m = (110) : (\bar{1}10) =$	126 15	126 10
$m : c = (110) : (001) =$	—	62 25
$b : c = (010) : (001) =$	89 57	90 0

The crystals are completely cleavable along {010}, readily so along {001}.

On {100} extinction occurs on orientation; on {010} under 28° with regard to the vertical side. The optical axial plane is {010}; at the border of the vision-sphere an optical axis is visible on {100}; the axial angle is small. The direction of the vertical axis is here the axis of the greatest elasticity.

On {100} etch excrescences were observable with a circumference of isorcelles trapezia, whose angular points appear to be connected by straight lines with a point situated in the centre; this point lies nearer to the smallest than to the largest of the two parallel sides of the trapezium. They agree with the indicated symmetry.

Fig. 3.



The specific gravity is 1,692, at 14° C.; the equivalent volume is, therefore, 113,4.

d. 1-4-Dichloro-2-Nitro-Benzene.

$C_6H_3.Cl.Cl.(NO_2)$ ; Melting point: 54°, 5 C.  
(4) (1) (2)

In most solvents this substance shows a very great crystallisation power, but measurable crystals are but rarely obtainable, as most of the individuals exhibit important geometrical deviations on account of the great softness of the material and often possess curved and very dull planes.

Some time ago the crystal form was incompletely determined by BODEWIG; he investigated crystals deposited from carbon disulphide but did not succeed in obtaining combinations admitting of a complete determination of the crystal parameters (Zeits. f. Kryst. 1. 589; Ann. Ch. Phys. (4). 15. 257).

From acetone I always obtained the largest crystals, sometimes some centimetres in length; they are quite of the prismatic type of the crystals investigated by BODEWIG and possess in addition a lateral prism; they exhibit, however, such considerable deviations and are generally so opaque that an accurate measurement is out of the question.

I succeeded best by crystallisation from ethyl-acetate mixed with a little carbon-tetrachloride; the pale sherry coloured crystals flattened towards {100} so obtained, are very well formed and admit of accurate measurement.

*Triclino-pinacoidal.*

$$a : b : c = 0,8072 : 1 : 0.8239$$

$$A = 79^{\circ} 33' \quad \alpha = 92^{\circ} 48'$$

$$B = 114^{\circ} 51\frac{1}{2}' \quad \beta = 112^{\circ} 51'$$

$$C = 58^{\circ} 35' \quad \gamma = 60^{\circ} 5'$$

Forms observed:  $a = \{100\}$ , predominant, well-reflecting, better than  $b = \{010\}$ , which form is also narrower;  $c = \{001\}$ , very lustrous and well developed;  $m = \{110\}$ , narrow but well-reflecting;  $q = \{011\}$ , narrow very lustrous;  $r = \{\bar{1}01\}$ , somewhat broader and yielding good reflexes.

The crystals are flattened along  $a$  and elongated in the direction of the  $c$ -axis.

	<i>Measured:</i>	<i>Calculated:</i>
$a : c = (100) : (001) =$	$* 65^{\circ} 8\frac{1}{2}'$	--
$a : b = (100) : (010) =$	$* 121 25$	--
$b : c = (010) : (001) =$	$* 100 27$	--
$a : r = (\bar{1}00) : (\bar{1}01) =$	$\gamma 50 12\frac{1}{2}'$	--
$c : q = (001) : (011) =$	$* 45 39$	--
$q : b = (011) : (010) =$	54 44	54 48'
$c : r = (001) : (\bar{1}01) =$	64 40 $\frac{1}{2}'$	64 40 $\frac{1}{2}'$
$m : b = (110) : (010) =$	75 23	75 19
$m : a = (110) : (100) =$	46 2	46 6
$r : q = (\bar{1}01) : (011) =$	51 50	51 35
$m : r = (\bar{1}\bar{1}0) : (\bar{1}01) =$	65 36	65 22
$m : q = (110) : (011) =$	62 54	63 3

The crystals are very completely cleavable towards  $\{001\}$ ; the plane of cleavage is very lustrous.

On  $\{100\}$  obtuse-angular extinction; its amount is small, only about  $7^{\circ} 40'$  in regard to the vertical side; in convergent light a dark hyperbole is noticed on this plane.

The specific gravity of the crystals is 1,696 at  $12^{\circ} \text{C.}$ ; the equivalent volume is, therefore, 113,20.

The topical axes are  $\chi : \psi : \omega = 4,8484 : 6,0065 : 5,1422$ .