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**Chemistry.** — “On some derivatives of Phenylcarbamic acid.”

By Dr. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH).

The following contains a crystallographic description of some derivatives, chiefly *nitroderivatives* of *phenylcarbamic acid*  $C_6H_5.NH.CO.OH$  which have been kindly presented to me by Prof. VAN ROMBURGH. The substances belonging to this series, which have been investigated are:

*Phenylcarbamic Methyl-ester.*

*Methylphenylcarbamic Methyl-ester.*

*1-4-Dinitromethylphenylcarbamic Methyl-ester.*

*1-2-4-Dinitromethylphenylcarbamic Methyl-ester.*

*1-2-4-6-Trinitromethylphenylcarbamic Methyl-ester. (α-Modification).*

*1-2-4-6-Trinitromethylphenylcarbamic Methyl-ester. (β-Modification).*

*1-2-4-Dinitromethylphenylcarbamic Aethyl-ester.*

*1-2-4-6-Trinitromethylphenylcarbamic Aethyl-ester.*

In addition, a description is given of *1-2-4-6-Methylphenylnitramine* m. p.  $127^\circ C.$ , which has been obtained from *1-2-4-Dinitromonomethyl-aniline* m. p.  $178^\circ C.$  by means of fuming nitric acid, which aniline is the product of decomposition of the two *Dinitromethylphenylcarbamic esters* on heating with strong hydrochloric acid <sup>1)</sup>, and which has been already described by me in the *Zeits. f. Kryst. Bd. 40 (1905). p. 119.*

### 1. Phenylcarbamic Methyl-ester.

$C_6H_5.NH.CO.O(CH_3)$ ; m. p.  $47^\circ C.$

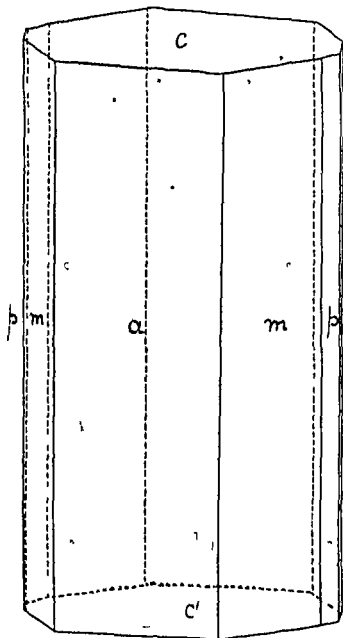


Fig. 1.

The compound crystallises best from alcohol and always in the form of colorless, elongated, rectangular little plates, which are very poor in combination forms.

*Rhombic bipyramidal.*

$$a : b = 1,5952 : 1.$$

The relation  $b : c$  cannot be determined on account of the absence of planes from the zones of  $(100,001)$ , and of  $(001,010)$ .

Forms observed:  $a = \{100\}$ , strongly predominating often vertically striped;  $p = \{110\}$ , very lustrous;  $m = \{120\}$ , narrow or totally wanting and sometimes as strongly developed as  $p$ ;  $b = \{010\}$ , indicated only a few times;  $c = \{001\}$ , reflects well.

<sup>1)</sup> VAN ROMBURGH. On the action of nitric acid on the esters methylphenylaminoformic acid. *Proc.* 29 Dec. 1900, Vol. III. p. 451.

|  | <i>Measured:</i> | <i>Calculated:</i>          |
|--|------------------|-----------------------------|
| $a : p = (100) : (110) = * 57^{\circ} 55'$ |                  | —                           |
| $a : m = (100) : (120) = 38 \ 31$          |                  | $38^{\circ} 34\frac{1}{2}'$ |
| $a : c = (100) : (001) = 90 \ 4$           |                  | 90 \ 0                      |
| $m : p = (120) : (110) = 19 \ 34$          |                  | 19 \ 24                     |
| $p : p = (110) : (\bar{1}10) = 64 \ 10$    |                  | 64 \ 10                     |
| $p : b = (110) : (010) = 32 \ 10$          |                  | 32 \ 5                      |

Completely cleavable towards {001} and towards {100}.

Orientated extinction on all planes in the vertical zone. The optical axial plane is {001} with  $a$  as acute diagonal. The axial angle is small, the dispersion fair with  $\rho > v$  around the  $a$ -axis.

The sp. gr. of the crystals is 1,251 at.  $19^{\circ}$ ; the equivalent volume 120,7.

## 2. Methyl-Phenylcarbamic Methyl-ester.

$C_6H_5 \cdot N(CH_3) \cdot CO \cdot O(CH_3)$ ; m.p.:  $44^{\circ} C$ .

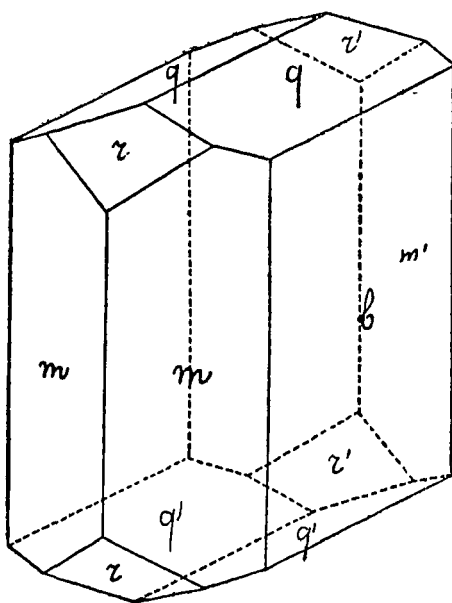


Fig. 2.

The compound crystallises from alcohol in large colourless crystals, which are frequently in clusters, often exhibit rather opaque planes and possess a peculiar camphor-like odour.

*Rhombic-bipyramidal.*

$a : b : c = 0,8406 : 1 : 0,3320$ .

Forms observed :

$b = \{010\}$ , strongly predominating;  $m = \{110\}$ , and  $q = \{011\}$ , both well developed and yielding sharp reflexes;  $r = \{201\}$ , fairly lustrous.

Different crystal-individuals exhibit not inconsiderable differences in the angular values.

|  | <i>Measured:</i> | <i>Calculated:</i>   |
|--|------------------|----------------------|
| $b : m = (010) : (110) = * 49^{\circ} 57'$     |                  | —                    |
| $b : q = (010) : (011) = * 71 \ 38$            |                  | —                    |
| $r : r = (\bar{2}01) : (\bar{2}01) = 103 \ 25$ |                  | $103^{\circ} 23'$    |
| $r : m = (201) : (110) = 61 \ 54$              |                  | $61 \ 40\frac{1}{3}$ |

Very completely cleavable towards  $b$ .

The optical axial plane {001} whilst  $b$  is the first diagonal. The axial angle is small, the dispersion strong and perhaps abnormal. It was not possible to properly characterise it with the means at my disposal.

The sp. gr. of the crystals is 1,296, at  $19^\circ$ ; the equivalent volume 127,31.

Topical axes :  $\chi : \psi : \omega = 5,1358 : 6,1099 : 4,0569$ .

On account of the symbol {201} the relation  $b : c = 1 : 0,6640$  has been taken.

### 3. 1-4-Nitro-Methyl-Phenyl-Carbamic Methyl-ester.

$C_8H_4(NO_2)_2 \cdot N(CH_3) \cdot CO \cdot O(CH_3)$ ; melting point :  $108^\circ C$ .  
(4) (1)

This compound crystallises from alcohol or benzene in the form of small delicate needles, or large, pale-sherry coloured, somewhat

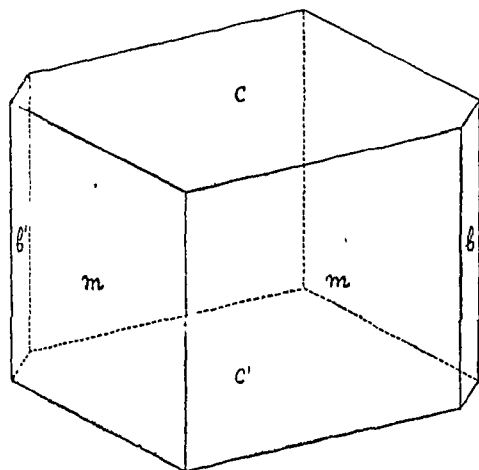


Fig. 3.

flat crystals, which, however, are very poor in planes, and, therefore, do not allow of a complete parameter-determination.

*Monoclinic-prismatic.*

$a : b = 0,6640 : 1$ .

$\beta = 70^\circ 58'$ .

Forms observed :

$c = \{001\}$  generally strongly predominating ;  $m = \{110\}$  well developed ;  $b = \{010\}$ , narrow. Often the planes of  $m$  and  $b$  are curved and the crystals exhibit greater anomalies in the angular

values.

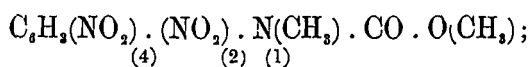
The habitus is mostly broadly flattened towards  $c$ , sometimes  $c$  and  $m$  are equally large and the habitus consequently becomes rhombohedral.

Very completely cleavable towards {001}.

The optical axial plane is probably {010}; on  $c$  one optical axis is visible on the border of the field of vision.

The sp. gr. of the crystals is 1,522 at  $14^\circ$ ; the equivalent-volume = 137,98.

## 4. 1-2-4-Dinitro-Methyl-Phenylcarbamic Methyl-ester.



m.p.: 98° C.

The best crystals are obtained from xylene. They are of a pale yellow colour and have the appearance of small, thick parallelogram-shaped crystals.

*Monoclinic-prismatic.*

$$a : b : c = 0,7597 : 1 : 1,0875.$$

$$\beta = 88^\circ 43\frac{1}{2}'.$$

Forms observed:  $b = \{010\}$ , predominating and very lustrous;  $r = \{\bar{1}01\}$ , broad and sharply reflecting;  $\omega = \{111\}$ , also broad and very lustrous;  $o = \{\bar{1}\bar{1}1\}$ , somewhat smaller than  $r$  but giving a good reflection;  $q = \{011\}$ , small and approximately measurable. The crystals are broadly flattened towards  $b$ .

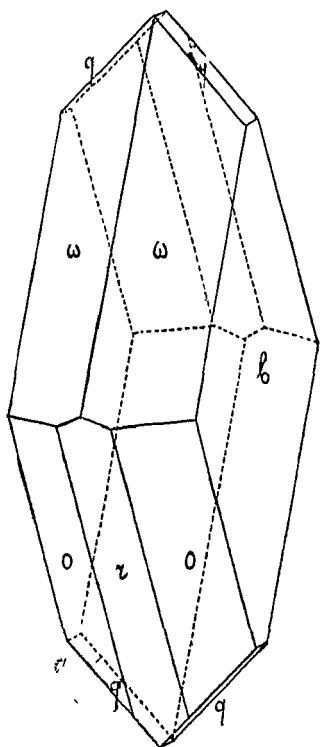


Fig. 4.

|  | <i>Measured:</i> | <i>Calculated:</i> |
|--|------------------|--------------------|
| $o : r = (\bar{1}\bar{1}1) : (\bar{1}01) =$                  | * 32° 44'        | —                  |
| $\omega : \omega = (111) : (\bar{1}\bar{1}1) =$              | * 64 22½         | —                  |
| $o : \omega = (\bar{1}\bar{1}1) : (111) =$                   | * 86 37½         | —                  |
| $b : \omega = (010) : (111) =$                               | 57 51            | 57° 49'            |
| $b : o = (010) : (\bar{1}\bar{1}1) =$                        | 57 0             | 57 16              |
| $\omega : q = (111) : (011) =$                               | 42 35 (about)    | 42 54              |
| $\omega : o = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}\bar{1}) =$ | 58 26            | 58 12              |
| $\omega : r = (\bar{1}\bar{1}\bar{1}) : (\bar{1}01) =$       | 74 12            | 74 24              |

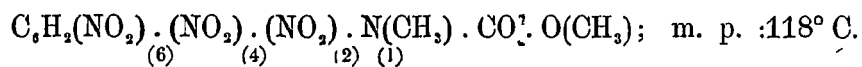
Cleavable towards  $\{\bar{1}\bar{1}1\}$ .

On  $\{010\}$ , the angle of extinction with regard to the side  $b : \omega$  is 22°; an axial image could not be observed.

The sp. gr. of the crystals is 1,506, at 14°; the equivalent volume = 169,32.

Topical axes:  $\chi : \psi : \omega = 4,4794 : 5,8963 : 6,4123$ .

## 5. 1-2-4-6-Trinitro-Methyl-Phenylcarbamic Methyl-ester.



This compound occurs in two modifications.

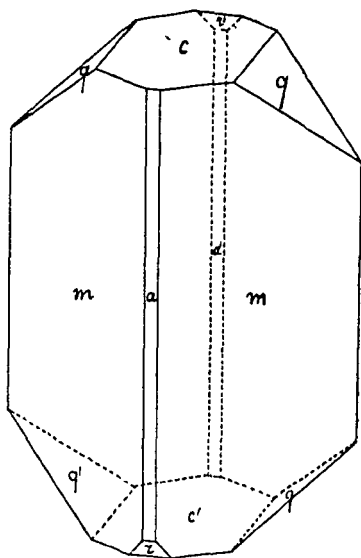
 *$\alpha$ -Modification.*

Fig. 5.

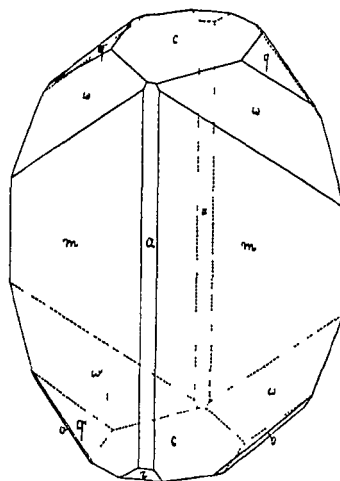


Fig. 6.

This  $\alpha$ -modification is the one usually deposited from the ordinary solvents, alcohol, acetone, benzene etc. The crystals described here have been obtained from acetone. They are colourless or of a pale sherry colour and very lustrous.

*Monoclinic-prismatic.*

$$a : b : c = 0,5758 ; 1 0,8382.$$

$$\beta = 75^\circ 41'.$$

Forms observed:  $m = \{110\}$ , broad and very lustrous;  $c = \{001\}$ , ideal reflection;  $q = \{011\}$ , large and very lustrous;  $\omega = \{121\}$ , generally broader than  $q$ , sometimes also narrower or even completely wanting;  $a = \{100\}$ , lustrous but narrow;  $r = \{\bar{1}01\}$  is often wanting but reflects well;  $o = \{\bar{1}21\}$  very narrow and dull.

|                           | <i>Measured:</i>      | <i>Calculated:</i> |
|---------------------------|-----------------------|--------------------|
| $a : c = (100) : (001) =$ | * $75^\circ 41'$      | —                  |
| $a : m = (100) : (110) =$ | * $29 \ 9\frac{1}{2}$ | —                  |
| $c : q = (001) : (011) =$ | * $39 \ 5$            | —                  |

|   | <i>Measured:</i>    | <i>Calculated:</i>  |
|---|---------------------|---------------------|
| $m : c = (110) : (001) =$                         | $77\ 32\frac{1}{2}$ | $77^{\circ}32'$     |
| $m : q = (\bar{1}\bar{1}0) : (011) =$             | $61\ 47$            | $61\ 39$            |
| $m : \omega = (110) : (121) =$                    | $26\ 30$            | $26\ 27$            |
| $a : \omega = (100) : (121) =$                    | $47\ 55\frac{1}{2}$ | $48\ 0$             |
| $\omega : c = (121) : (001) =$                    | $57\ 43$            | $57\ 42$            |
| $\omega : q = (121) : (011) =$                    | $35\ 16$            | $35\ 12$            |
| $m : q = (\bar{1}\bar{1}0) : (011) =$             | $81\ 40$            | $81\ 59$            |
| $m : o = (\bar{1}\bar{1}0) : (\bar{1}\bar{2}1) =$ | $34\ 39\frac{1}{2}$ | $34\ 37\frac{1}{2}$ |
| $o : q = (\bar{1}\bar{2}1) : (011) =$             | $46\ 19\frac{1}{2}$ | $46\ 22$            |
| $c : r = (001) : (\bar{1}01) =$                   | $65\ 38\frac{1}{2}$ | $65\ 36$            |
| $a : r = (\bar{1}00) : (\bar{1}01) =$             | $38\ 51\frac{1}{2}$ | $38\ 43$            |
| $m : r = (\bar{1}\bar{1}0) : (\bar{1}01) =$       | $47\ 2$             | $47\ 3$             |
| $r : q = (\bar{1}01) : (011) =$                   | $70\ 59\frac{1}{2}$ | $71\ 17\frac{3}{4}$ |

No distinct plane of cleavability was found; perhaps there is one present parallel to  $m$ .

The symmetric extinction on  $\{110\}$  with regard to the side  $(110) : (\bar{1}\bar{1}0)$ , etc. amounts to about  $18^{\circ}$ ; on  $a$  and  $c$  it is normally orientated. The average refraction is a trifle greater than that of  $\alpha$ -monobromo-naphthalene.

The sp. gr. gravity of the crystals is 1,612, at  $19^{\circ}$ ; the equivalent volume is 186,10.

Topical axes:  $\chi : \psi : \omega = 4,2360 : 7,3555 : 6,1655$ .

#### 5b. Trinitro-Methyl-Phenylcarbamic Methylester.

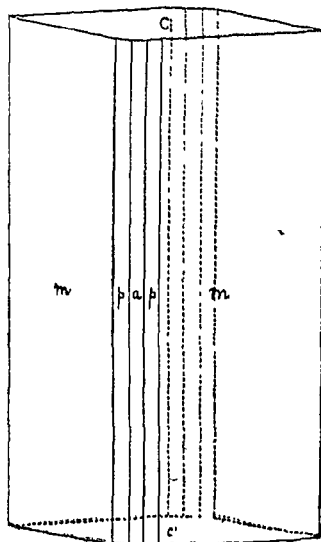


Fig. 7.

*$\beta$ -Modification.* When long kept, the crystals of the  $\alpha$ -modification turn a little darker, somewhat more orange-yellow. The symmetry and all the angles of the  $\alpha$ -modification are, however, preserved.

Sometimes, the alcohol deposits long needles together with crystals of the  $\alpha$ -modification. These needles have an orange colour; at about  $105^{\circ}$  they again turn yellow and then melt just a little below  $118^{\circ}$ . Although it is not as yet quite clear in what relation these needles stand to the crystals, it is nevertheless certain, that they represent a second less stable modification of the compound. The meltingpoint of the crystals of the  $\alpha$ -modification obtained from various solvents, or after heating in diffe-

rent ways, fluctuates between  $114^\circ$  and  $118^\circ$ . A further investigation will be necessary to see what really takes place here.

*Rhombic-bipyramidal.*

$$a : b = 0,6596 : 1.$$

The relation  $b : c$  cannot be determined, for want of the necessary terminal planes.

Forms observed:  $m = \{110\}$ , broad and lustrous;  $c = \{001\}$ , very sharply reflecting;  $a = \{100\}$ , narrow, well reflecting;  $p = \{310\}$ , very narrow and yielding bad reflexes.

*Measured:    Calculated:*

|                                 |                             |                 |
|---------------------------------|-----------------------------|-----------------|
| $a : m = (100) : (110) =$       | $* 33^\circ 24\frac{1}{2}'$ | —               |
| $m : m = (110) : (\bar{1}10) =$ | $113 11\frac{1}{2}$         | $113^\circ 11'$ |
| $m : c = (110) : (001) =$       | $90 1$                      | $90 0$          |
| $m : p = (110) : (310) =$       | $20 17$ (about)             | $21 0$          |
| $p : a = (310) : (100) =$       | $13 2$ (about)              | $12 24$         |

Perfectly cleavable towards  $\{001\}$ .

The optical axial plane is  $\{001\}$ ; the first diagonal is the  $a$ -axis. The apparent axial angle is in  $\alpha$ -monobromonaphthalene about  $86^\circ$ ; extraordinary strong dispersion with  $\rho > v$ , round the first bissectrix. Orientated extinction everywhere in the vertical zone.

The sp. gr. of the needles is 1,601, at  $19^\circ$ ; the equivalent volume = 187,32.

#### 6. 1-2-4-Dinitro-Methyl-Phenylcarbamic Ethyl-ester.

$C_6H_3(NO_2)_4 \cdot (NO_2)_2 \cdot N_{(1)}(CH_3) \cdot CO \cdot O(C_2H_5)$ ; m. p.  $112^\circ C$ .

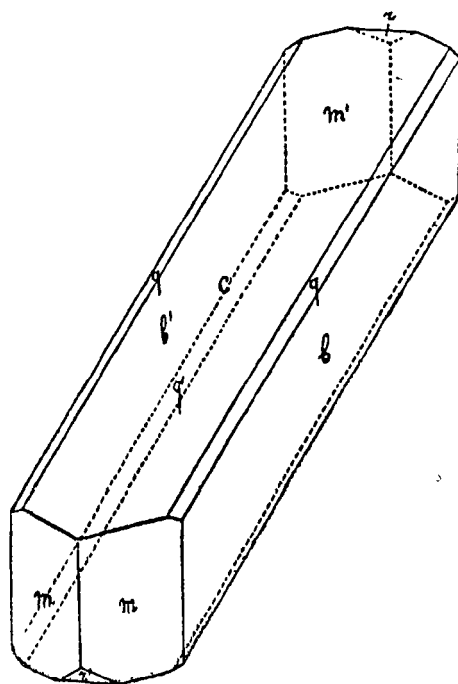


Fig. 8.

This compound crystallises from a mixture of benzene and ligroine; in the form of large, colourless, very lustrous crystals represented in fig 8.

*Monoclinic-prismatic.*

$$a : b : c = 0,6525 : 1 : 0,7035.$$

$$\beta = 69^\circ 59'.$$

Forms observed:  $c = \{001\}$ , predominating and very lustrous;  $b = \{010\}$ , about as broad as  $c$  and sharply reflecting;  $m = \{110\}$ , well reflecting and properly developed, sometimes with delicate striping parallel to  $m : c$ ;  $q = \{011\}$ , narrower but readily measurable;  $r = \{1\bar{0}1\}$ , very distinctly developed and yielding



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sharp reflexes,  $p \cong \{120\}$ , very narrow and dull; often absent altogether.

|  | <i>Measured:</i> | <i>Calculated:</i> |
|--|------------------|--------------------|
| $m : m = (100) : \bar{1}10 = '63^\circ 1\frac{1}{2}'$          |                  | —                  |
| $m : c = (110) : (001) = '73 2$                                |                  | —                  |
| $q : c = (011) : (001) = '33 28$                               |                  | —                  |
| $q : b = (011) : (010) = 56 32$                                |                  | 56° 32'            |
| $m : b = (110) : (010) = 58 26\frac{1}{2}$                     |                  | 58 29              |
| $m : p = (110) : (120) = 19 12$                                |                  | 19 17              |
| $p : b = (120) : (010) = 39 23\frac{1}{2}$                     |                  | 39 12              |
| $r : c = (\bar{1}01) : (001) = 58 10$                          |                  | 58 5               |
| $r : m = (1\bar{0}\bar{1}) : (110) = 58 12$                    |                  | 58 18              |
| $m : q = (110) : (01\bar{1}) = 57 58\frac{1}{2}$ (circa)       |                  | 58 41              |
| $q : r = (01\bar{1}) : (\bar{1}01) = 63 41\frac{1}{2}$ (circa) |                  | 63 22              |
| $c : b = (001) : (010) = 89 58$                                |                  | 90 0               |

Very perfectly cleavable towards  $\{001\}$ ; like "glimmer" the crystals may be reduced to very delicate lamellae.

On  $\{001\}$  orientated extinction; on  $\{110\}$  the inclination of the one elasticity-axis towards the vertical axis amounts to  $19^\circ$ ; on  $\{010\}$ :  $27^\circ$  with regard to the side  $b : c$ , in the acute angle  $\beta$ . The axial plane is, probably, situated perpendicularly to  $\{010\}$ . By means of  $\alpha$ -monobromonaphthalene etched figures were obtained on  $m$ ,  $c$  and  $b$ , which are in accordance with the indicated symmetry.

The sp. gr. of the crystals is 1,461 at  $19^\circ$  C.; the equivalent volume = 184,12.

Topical axes:  $\chi : \psi : \omega = 4,9130 : 7,5296 : 5,2970$ .

#### 7. 1-2-4-6-Trinitromethylphenylcarbamic Ethyl-ester.

$C_6H_2(NO_2)_{(6)} \cdot (NO_2)_{(4)} \cdot (NO_2)_{(2)} \cdot N(CH_3)_{(1)} \cdot CO \cdot O(C_2H_5)$ ; m. p.  $65^\circ$  C.

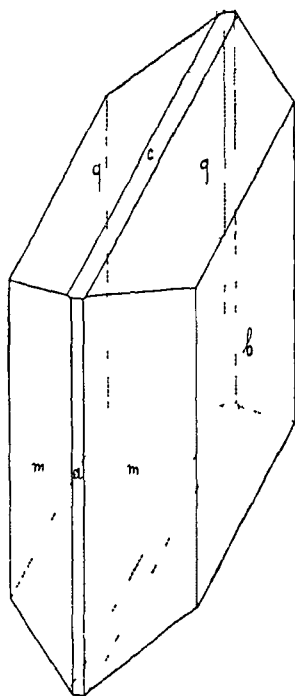


Fig. 9.

The crystals which have been measured are derived from a mixture of benzene and ligroine.

Delicate, very transparent, flat, pale sherry-coloured needles which possess a strong lustre.

*Monoclinic-prismatic.*

$$a : b : c = 0,9759 : 1 : 0,3929$$

$$\beta = 67^{\circ}7'.$$

Forms observed:  $b = \{010\}$ , yielding ideal reflexes and well developed:  $o = \{\bar{1}21\}$ ,  $a = \{100\}$ , and  $c = \{001\}$ , very narrow and dull;  $m = \{110\}$ , broad and very lustrous;  $q = \{011\}$ , well developed and yielding sharp reflexes; an orthodome  $\{h\ 0\ k\}$  is indicated but not measurable. The needles are elongated towards the  $c$ -axis and somewhat flattened towards  $\{010\}$ .

*Measured:      Calculated:*

|  |                            |
|--|----------------------------|
| $m \cdot m = (110) : (110) = 83^{\circ} 55'$           | —                          |
| $m \cdot q = (110) : (011) = 60 \quad 2$               | —                          |
| $q \cdot q = (011) : (0\bar{1}1) = 39 \quad 48$        | —                          |
| $m \cdot b = (110) : (010) = 48 \quad 3$               | $48^{\circ} 1\frac{1}{2}'$ |
| $b \cdot q = (010) : (011) = 70 \quad 6$               | $70 \quad 6$               |
| $m \cdot q = (\bar{1}10) : (\bar{0}11) = 119 \quad 58$ | $119 \quad 58$             |
| $m \cdot o = (\bar{1}10) : (\bar{1}21) = 64 \quad 46$  | $65 \quad 2$               |
| $o \cdot q = (\bar{1}21) : (011) = 27 \quad 32$        | $27 \quad 29$              |
| $q \cdot m = (011) : (\bar{1}10) = 87 \quad 42$        | $87 \quad 28$              |
| $m \cdot a = (110) : (100) = 41 \quad 57$              | $41 \quad 57\frac{1}{2}$   |

A distinct cleavability was not observed.

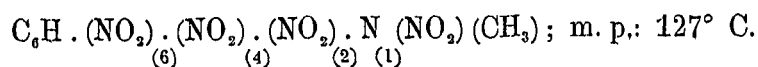
The angle of extinction on  $b$  is  $9^{\circ}$  with regard to the vertical axis, in the acute angle  $a : c$ ; on  $m$  it is about  $6\frac{1}{2}^{\circ}$ .

In oil of cloves, solution figures were obtained as represented in fig. 8; they are in accordance with the found symmetry.

The sp. gr. of the crystals is  $= 1,471$  at  $14^{\circ}$ ; the equivalent volume  $= 194,42$ .

Topical axes:  $\chi = \psi : \omega = 7,9976 : 8,1950 : 3,2198$ .

## 8. 1-2-4-6-Trinitrophenylmethylnitramine.



The compound is obtained from benzene + acetone in the shape of small, very strongly refracting, pale sherry-coloured needles, which possess a strong lustre and are, geometrically, very well built.

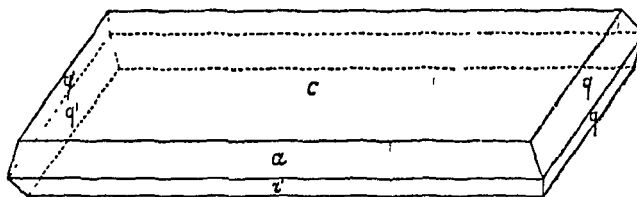


Fig. 10.

*Monoclinic prismatic.*

$$a : b : c = 2,7823 : 1 : 3,5242.$$

$$\beta = 75^\circ 31\frac{1}{2}'.$$

Forms observed:  $c = \{001\}$ , most strongly developed of all;  $a = \{100\}$  and  $r = \{\bar{1}01\}$ , both strongly reflecting;  $q = \{011\}$  somewhat more opaque.

|                                       | <i>Measured:</i>            | <i>Calculated:</i>  |
|---------------------------------------|-----------------------------|---------------------|
| $a : c = (100) : (001) =$             | $* 75^\circ 31\frac{1}{2}'$ | —                   |
| $a : r = (\bar{1}00) : (\bar{1}01) =$ | $* 43 36\frac{1}{2}'$       | —                   |
| $c : q = (001) : (011) =$             | $* 73 40'$                  | —                   |
| $c : r = (001) : (\bar{1}01) =$       | $60 53'$                    | $60^\circ 53'$      |
| $q : q = (011) : (0\bar{1}1) =$       | $32 32'$                    | $32 40'$            |
| $a : q = (100) : (011) =$             | $85 54'$                    | $85 58\frac{1}{2}'$ |

A distinct cleavability was not found.

Optical axial plane is  $\{010\}$ ; on  $\{001\}$  one axis is placed nearly perpendicular. The double-refraction is moderate and negative; extraordinarily great dispersion with  $\rho > v$ .

The sp. gr. of the little crystals is: 1,570, at  $19^\circ$ ; the equivalent volume = 182,16.

Topical axes:  $\chi : \psi : \omega = 7,4485 : 2,6772 : 9,4347$ .