Chemistry. — *"On the Crystalforms of some position-isomeric Dinitrotoluenes"*. By Prof. F. M. JAEGER.

(Communicated at the meeting of October 31, 1925).

§ 1. In the following article are communicated the results of the crystallographic measurements made with a number of position-isomeric Dinitrotoluenes, which had been were prepared by Dr. H. A. SIRKS [1]) and given to me by this author for the purpose mentioned. It appeared possible to obtain five of the six possible isomerides in a form suitable for measurement. For the purpose of comparison also some measurements are considered here, made with some other *nitro*-derivatives of *toluene* by BODEWIG [2]), CALDERON [2]) and FRIEDLÄNDER [3]).

§ 2. 1-2-3-*Dinitrotoluene*: $C_6H_3(NO_2)_2$; Mpt. 60° C.

This substance was obtained from ether in the shape of small, almost colourless tabular crystals. They are well built and show constant angular values.

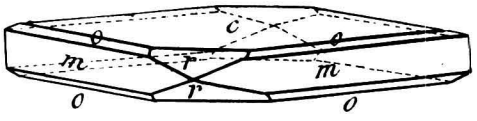

Fig. 1.

Rhombic-bipyramidal.

$a : b : c = 0{,}6352 : 1 : 0{,}3721$.

Forms observed: $c = \{001\}$, predominant, very lustrous; $m = \{110\}$, well developed and yielding very sharp images; $r = \{101\}$, large and well reflecting; $o = \{111\}$, extremely narrow, mostly absent, and yielding only faint reflections. The habit of the crystals is tabular parallel to $\{001\}$.

Angular values:	*Observed:*		*Calculated:*	
$c : r = (001) : (101) =$*	30°	21½′	—	
$m : m = (110) : (1\bar{1}0) =$*	64	51	—	
$m : c = (110) : (001) =$	90	0	90°	0′
$m : m = (110) : (\bar{1}10) =$	115	9	115	9
$r : r = (101) : (10\bar{1}) =$	119	25	119	7
$m : o = (110) : (111) =$	36	39½	36	58
$o : c = (111) : (001) =$	53	20½	53	2½

No distinct cleavability was found.

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[1]) H. A. SIRKS, Dissertatie, Groningen, (1906).

[2]) C. BODEWIG, Zeits. f. Kryst., **3**, 388, (1879); L. CALDERON, ibid., **4**, 235, (188

[3]) P. FRIEDLÄNDER, Zeits. f. Kryst., **3**, 170, 173, (1879).

§ 3. 1-2-4-*Dinitrotoluene*; Mpt.: 71° C.

From a mixture of ether and alcool this compound was obtained in colourless, flat needles.

Monoclinic-prismatic.

$$a : b : c = 0{,}8553 : 1 : 0{,}5236;$$
$$\beta = 84° \; 37\tfrac{1}{2}'.$$

Forms observed: $m = \{110\}$ and $b = \{010\}$, large and very lustrous; $a = \{100\}$, much narrower than either of these forms, but yielding good reflections; $r = \{101\}$, large, but dull; $c = \{001\}$, small and yielding only faint images; $o = \{111\}$, narrow, but very lustrous; $p = \{120\}$, extremely narrow. The shape of the crystals is prismatic parallel to the *c*-axis.

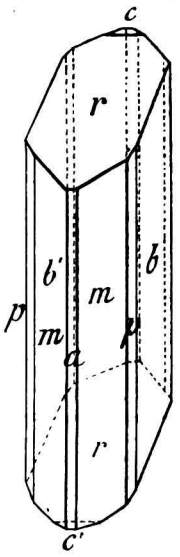

Fig. 2.

Angular Values:	*Measured:*		*Calculated:*	
$m : r = (110) : (101) =$	* 63°	$52\frac{1}{2}'$	—	
$m : b = (110) : (010) =$	* 49	35	—	
$r : o = (101) : (111) =$	* 39	48	—	
$m : o = (110) : (111) =$	76	$19\frac{1}{2}$	76°	$19\frac{1}{2}'$
$a : r = (100) : (101) =$	54	38	54	40
$a : m = (100) : (110) =$	40	25	40	25
$p : b = (120) : (010) =$	29	$49\frac{1}{2}$	30	25
$p : n = (120) : (110) =$	19	26	19	10
$c : r = (001) : (101) =$	29	$47\frac{1}{2}$	29	$57\frac{1}{2}$
$a : c = (100) : (001) =$	84	25	84	$37\frac{1}{2}$
$c : b = (001) : (010) =$	90	0	90	0
$o : b = (111) : (010) =$	62	35	62	28

No distinct cleavage could be observed.

The optical axial plane is perpendicular to $\{010\}$.

This substance was also studied by BODEWIG [1]; with his (pale yellow) crystals this author found: $a : b : c = 0{,}8593 : 1 : 0{,}5407$; $\beta = 85° \; 12'$. Perhaps small traces of impurities are responsible for the differences of angular values compared with those here observed.

§ 4. 1-2-6-*Dinitro-toluene*; Mpt. 66° C.

From ethylacetate this isomeride was obtained as big, flat, and colourless crystals, showing constant angular values and permitting accurate measurements [2].

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[1]) C. BODEWIG, loco cit., p. 389.

[2]) See also: K. HEYDRICH, Zeits. f. Kryst., **48**, 268, (1911). The melting-point mentioned there is 6° too low.

Rhombic-bipyramidal (pseudohexagonal).

$a : b : c = 0{,}5725 : 1 : 0{,}5324.$

Forms observed: $m = \{110\}$, broad highly lustrous; $b = \{010\}$, also well developed and yielding good reflections; $r = \{101\}$, narrow, but eminently reflecting; $q = \{011\}$, also strongly lustrous; $s = 012$, narrow, yielding sharp images.

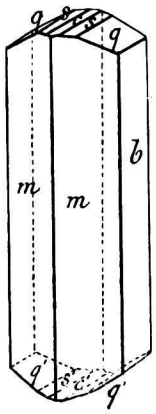

Fig. 3.

Angular values:	*Measured:*		*Calculated:*	
$m : m = (110) : (1\bar{1}0) =$	* 59°	59′	—	
$b : q = (010) : (011) =$	* 61	58	—	
$b : m = (010) : (110) =$	60	12½	60°	12½′
$q : s = (011) : (012) =$	13	6	13	7½
$s : c = (012) : (001) =$	14	57	14	54½
$m : q = (110) : (011) =$	76	23½	76	29½

Cleavage distinct parallel to $\{001\}$.

The shape of the crystals is elongated parallel to the *c*-axis, either parallel to $\{010\}$, or to a pair of faces of $\{110\}$. Sometimes hexagonally limited plates were obtained, showing only $\{001\}$, with *m* and *b* as bordering facets. The plane of the optical axes is $\{100\}$, with *c*-axis as first bissectrix.

§ 5. 1-3-4-*Dinitro-toluene*; Mpt. 60° C.

From a mixture of benzene and ethyl-alcool the substance crystallizes in very thin, transparent needles, which mostly show no limiting faces at the top, beyond the basis $\{001\}$. Rarely, however, a form $q = \{011\}$ was observed, only very small.

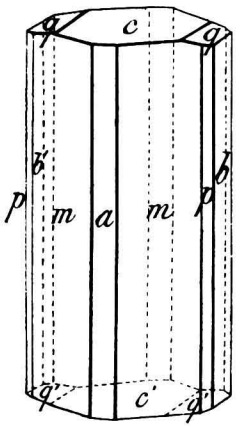

Fig. 4.

Monoclinic-prismatic.

$a : b : c = 0{,}8320 : 1 : 0{,}2465;$

$\beta = 88° 25'.$

Forms observed: $a = \{100\}$, $m = \{110\}$ and $p = \{120\}$, all three about equally broad and yielding good images; $b = \{010\}$, somewhat narrower $c = \{001\}$, well reflecting; $q = \{011\}$, small and giving only faint reflections. The crystal-habitus is elongated parallel to the *c*-axis.

Angular values:	*Observed:*		*Calculated:*
$m : b = (110) : (010) =$	* 50°	15′	—
$q : p = (011) : (\bar{1}20) =$	* 79	3	—
$q : c = (011) : (001) =$	* 13	50½	

Angular Values:	*Observed:*	*Calculated:*
$c:p = (001):(120) =$	89° 8½′	89° 11′
$a:c = (100):(001) =$	88 27	88 25
$c:b = (001):(010) =$	90 0	90 0
$a:m = (100):(110) =$	39 45	39 45
$m:p = (110):(120) =$	19 18	19 14½

No distinct cleavage could be observed.

The extinction on *m*, *p* and *b* differs only inappreciably from 90°.

§ 6. It may be remarked in connection with the measurements of the isomeric 1-2-4- and 1-3-4-*Dinitrotoluenes*, which both are derivatives of *p-Nitrotoluene*, that this last (Mpt. : 54° C.), is *rhombic-bipyramidal*, with: $a:b:c = 0{,}9107:1:1{,}0965$ and the forms: {110}, {011}, {211}, {001}, and {010}. The crystals are perfectly cleavable parallel to {010}. The plane of the optical axes is parallel to {100}, with the *c*-axis as first bissectrix of negative character. The dispersion is: $\varrho > v$.

Furthermore measurements are made of: 1-2-4-6 and 1-3-4-6-*Trinitrotoluene*; both these compounds are also *rhombic-bipyramidal*, 1-2-4-6-*trinitrotoluene* (Mpt.: 82° C.) has the parameters: $a:b:c = 0{,}7586:1:0{,}5970$, and exhibits the forms: {110}, {010}, {210} and {011}. The optical axial plane is {001}, the double refraction is negative. 1-3-4-6-*Trinitrotoluene* (Mpt.: 104° C.) possesses the axial ratio: $a:b:c = 0{,}9373:1:0{,}6724$, and shows the forms: {010}, {111}, {120}, {021} and {001}. This compound has a positive double refraction; the plane of the optical axes is {100}.

From these data it is clear that there does not exist a close form-analogy between the *mono-*, *di-* and *tri-nitro*-derivatives of *toluene*; at the utmost, one might speak of some relation in the value $b:c$ in the 1-2-4-derivative and in *p-Nitrotoluene*, if for the *c*-axis half the measured value be taken, while the angle β decreases from 90° to 84° 37½′ Then also a certain analogy can be seen in the relations $b:c$ of these two compounds with the 1-2-6- and 1-3-5-derivative (see below), although, as a fact these isomerides cannot be considered to be derivatives of *p-Nitrotoluene*. As a final result, therefore, it must be considered to be artificial to indicate any crystallographical relationship here, — the more so, as the 1-3-4-derivative on the other hand does not show any relation of this kind with respect to the substances mentioned in the above.

§ 7. 1-3-5-*Dinitro-toluene*; Mpt.: 93° C.

From a mixture of benzene and carbodisulphide, peculiarly shaped individuals were obtained, being wedge-shaped. They appeared, however, completely identical with the monoclinic crystals, obtained by BARNER [1]) from a mixture of benzene and acetic acid. They are bordered by {001}, two planes of {110} and two planes of {1$\bar{1}$1}, i. e. {1$\bar{1}$1} and {$\bar{1}\bar{1}$1}, and

[1]) F. BARNER, Zeits. f. Kryt., **9**, 300 (Ref.).

also by a number of strongly curved faces, giving the shape of a lance-point to the crystals dealt with here (Fig. 5).

Monoclinic-prismatic (*pseudo-rhombic*).

$a : b : c = 0{,}4691 : 1 : 0{,}5276$;

$\beta = 89° 51'$.

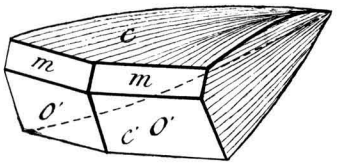

Fig. 5.

Forms observed: $o' = \{11\bar{1}\}$, rather large and well reflecting; $m = \{110\}$, narrower than o', also lustrous; $c = \{001\}$, large, is striated parallel to the edge (001) : (010). The indices of the curved faces were not determinable.

Angular Values:	*Observed:*	BARNER:	*Calculated:*
$c : m = (001) : (110) =$	* 89° 50′	89° 50′	—
$m : m = (110) : (1\bar{1}0) =$	* 50 12	50 15½	—
$m : o' = (110) : (11\bar{1}) =$	* 38 51	38 53	—
$o' : o' = (11\bar{1}) : (\bar{1}1\bar{1}) =$	38 41	38 41	38° 41′
$c : o' = (00\bar{1}) : (11\bar{1}) =$	51 18	51 15	51 22

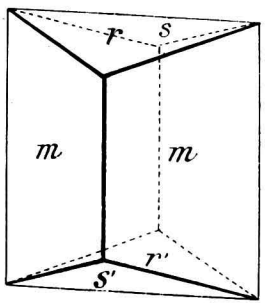

Fig. 6.

No distinct cleavability present.

The plane of the optical axes is perpendicular to $\{010\}$; on m the extinction is almost normally orientated. If this compound is recrystallized from ethyl-acetate, beautiful transparent crystals of the shape of Fig. 6 are obtained, which, however, soon become dull and opaque.

Monoclinic-prismatic.

$a : b : c = 0{,}7143 : 1 : 0{,}3853$;

$\beta = 73° 58½'$.

Forms observed: $m = \{110\}$ and $r = \{101\}$, large and highly lustrous; $s = \{\bar{1}01\}$, somewhat narrower than r, but well reflecting; $b = \{010\}$, rather narrow, but yielding very sharp reflections. The habitus of the crystals is short-prismatic along the c-axis.

Angular Values:	*Observed:*	*Calculated:*
$m : m = (110) : (1\bar{1}0) =$	* 68° 65½′	—
$m : r = (110) : (101) =$	* 57 46	—
$r : s = (101) : (\bar{1}01) =$	* 55 38	—
$m : b = (110) : (010) =$	55 32	55° 32′

No distinct cleavage was found.

Evidently no direct morphotropic relations exist between these crystals and those of the pure substance.

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