

The aspect is short prismatic in the direction of the *c*-axis, occasionally also isometrically developed.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) = *$	$60^{\circ} 13\frac{1}{2}'$	—
$a : r = (110) : (101) = *$	$67 51\frac{1}{2}'$	—
$m : m = (110) : (\bar{1}10) =$	$59 33$	$59^{\circ} 33'$
$r : r = (101) : (\bar{1}01) =$	$44 17$	$44 17$
$r : m = (101) : (110) =$	$79 10$	$79 12\frac{3}{4}$
$o : m = (523) : (110) = \text{ca.}$	$50 56$	$51 51$
$o : o = (523) : (\bar{5}23) = \text{ca.}$	$48 50$	$49 12\frac{1}{2}$
$o : o = (523) : (5\bar{2}3) =$	$117 30$	$117 0$

No distinct cleavage was observed.

§ 5. There is evidently no distinct form-analogy present between the two isomeric *chloro-tetracetyl-d-fructoses*, in contradiction to what was formerly stated in the case of both α - and β -*pentacetyl-d-fructoses*. The substitution of a Cl-atom for hydrogen, has evidently, however, not a lowering of the degree of symmetry of the original substances as a consequence, all four acetyl-derivatives being *rhombic-bisphenoidal*. However, from the results obtained, it appears still to be impossible to demonstrate a more intimate analogy of the crystal-forms of the α - and β -derivatives of this series and that studied formerly.

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Chemistry. — “On the Crystalforms of some Substituted Amides of *Para-Toluenesulphonic Acid*.” By Prof. F. M. JAEGER.

(Communicated at the meeting of June 26, 1920).

§ 1. In the following the results are communicated of an investigation concerning the crystallographical properties of a series of substituted *amides* derived from *p-toluene-sulphonic acid*¹⁾, already prepared by Prof. VAN ROMBURGH in 1902. These preparations, which in general occur in beautiful crystals, were ceded to me a long time ago by the said chemist for the purpose indicated; but the results of these measurements have not been published hitherto.

To colleague VAN ROMBURGH's benevolence I am indebted also for some still lacking data on the specific weight of several of these substances.

In the text occasionally attention has been drawn to some regularities of the crystalforms of these derivatives, which, from a chemical standpoint, are closely related to each other; a review of the numerical data is, moreover, added to this paper at the end. Distinct relations in the crystalforms of these derivatives have, however, not been found in great number, notwithstanding their close chemical relationship.

§ 2. I. Nitro-*p*-Toluene-sulpho-amide.

This substance, which melts at 141° C., crystallizes from ethyl-alcohol in big, very transparent crystals, which often possess curved

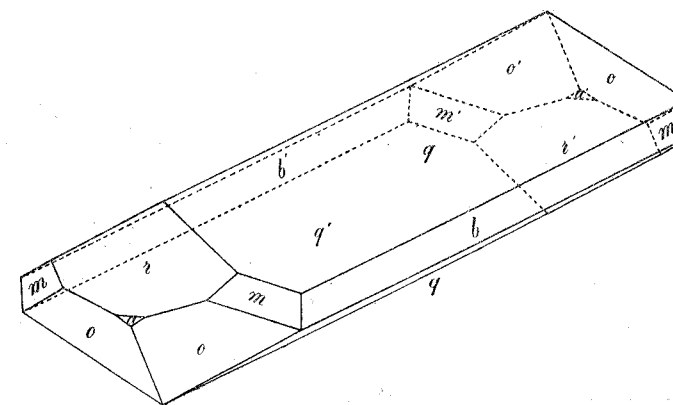


Fig. 1. Nitro-*p*-Toluene-sulpho-amide.

¹⁾ Cf. also: P. VAN ROMBURGH, *Proceed. Acad. of Sciences Amsterdam*, Februari, (1902).

faces, making the measurements rather difficult. From ethylacetate we obtained occasionally also great, hexagonally bounded, tabular individuals. The most exact measurements were made with very small, almost colourless crystals, showing very constant angular values.

Although they belong, according to their optical properties, to the monoclinic system, their angle β , however, does not differ from 90° .

Monoclinic-prismatic; pseudo-rhombic.

$$a : b : c = 1,2289 : 1 : 1,1812.$$

$$\beta = 90^\circ.$$

Forms Observed: $q = \{012\}$, predominant and yielding perfect reflexes; $r = \{101\}$, large and strongly reflecting; $m = \{110\}$, smaller, but well developed and lustrous; $b = \{010\}$, narrow and dull, often absent; $o = \{\bar{2}12\}$, well developed and lustrous; $a = \{100\}$, very small and dull, but at least measurable; finally an extremely small pyramid $x = \{\bar{7}11\}$ (?) was observed, which, however, was mostly absent and very badly reflecting. The aspect of the crystals is thick-prismatic parallel to q , with elongation in the direction of the a -axis; however, the crystals are often most irregularly distorted. Ordinarily r is present only with a single face.

Angular Values: *Observed:* *Calculated:*

$q : r = (012) : (101) = *$	$51^\circ 38\frac{1}{2}'$	—
$m : q = (110) : (012) = *$	$66\ 46$	—
$q : q = (012) : (0\bar{1}2) =$	$61\ 3$	$61^\circ\ 8'$
$q : b = (012) : (010) =$	$59\ 29$	$59\ 26$
$q : a = (012) : (100) =$	$90\ 0$	$90\ 0$
$o : o = (\bar{2}12) : (\bar{2}\bar{1}2) =$	$46\ 4\frac{1}{2}$	$46\ 8$
$o : q = (\bar{2}12) : (012) =$	$39\ 34\frac{1}{2}$	$39\ 37$
$o : q = (\bar{2}12) : (0\bar{1}2) =$	$67\ 59$	$68\ 10$
$m : o = (\bar{1}10) : (\bar{2}12) =$	$45\ 2$	$45\ 4$
$o : r = (\bar{2}12) : (101) =$	$23\ 4$	$23\ 4$
$m : q = (110) : (011) =$	$66\ 50$	$66\ 46$
$a : x = (\bar{1}00) : (\bar{7}11) =$	$18\ 48$	$19\ 3$

There is a distinct cleavage parallel to $\{010\}$.

Although the angle β does not differ appreciably, the optical properties prove, however, that the compound has monoclinic symmetry: on $\{012\}$ the extinction-angle is about 23° with respect to the a -axis; in the same way the extinction-angle on $\{010\}$ is about 42° with respect to the a -axis. The optical axial plane is probably parallel to $\{010\}$.

The specific weight of the crystals at 15° C. is: 1,612; the equivalent-volume is therefore: 133,99. The topical parameters are calculated to: $\chi : \psi : \omega = 5,5537 : 4,5194 : 5,3383$.

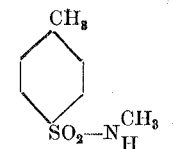
§ 3. Comparing the axial ratio with the parameters of the three isomeric *toluene-sulphonamides* themselves, their form-relationship becomes very clear, if only the interpretation is made somewhat deviating from that given in the literature¹⁾.

Adopting the symbols of the different combination-forms, as given by WEIBULL, we can give the following survey of the modified data:

<i>Ortho-toluene-sulphonamide</i> ; mpt: $156^\circ,3$ C. Tetragonal-bipyramidal. $p = \{110\}$; $v = \{111\}$; $o = \{113\}$; $u = \{313\}$.	$a : a : c = 1,000 : 1 : 1,0332$; $\beta = 90^\circ$.
<i>Meta-toluene-sulphonamide</i> ; mpt: 108° C. Monoclinic-prismatic; pseudo-tetragonal. $a = \{100\}$; $b = \{010\}$; $m = \{210\}$; $o = \{112\}$; $s = \{\bar{1}12\}$; $\omega = \{122\}$; $r = \{\bar{1}02\}$.	$a : b : c = 1,0453 : 1 : 1,0333$; $\beta = 88^\circ 27\frac{1}{2}'$.
<i>Para-toluene-sulphonamide</i> ; mpt: $137^\circ,5$ C. Monoclinic-prismatic. $b = \{010\}$; $p = \{011\}$; $o = \{\bar{3}12\}$; $v = \{310\}$; $r = \{302\}$.	$a : b : c = 1,2016 : 1 : 0,9364$; $\beta = 87^\circ 29'$.
<i>Nitro-p-toluene-sulphonamide</i> ; mpt: 141° C. Monoclinic-prismatic; pseudo-rhombic. $a = \{100\}$; $b = \{010\}$; $q = \{012\}$; $m = \{110\}$; $r = \{101\}$; $o = \{\bar{2}12\}$.	$a : b : c = 1,2289 : 1 : 1,1812$; $\beta = 90^\circ$.

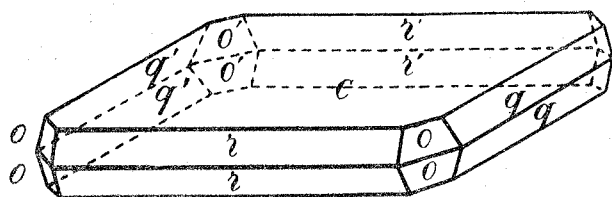
§ 4. II. p-Toluene-sulpho-methylamide.

This substance, which has the formula:



and which melts at 76° C., crystallizes from alcohol in the form of very thin, transparent, colourless, rectangular little plates.

¹⁾ M. WEIBULL, Zeit. f. Kryst. u. Miner. **15**, 251. (1889); O. MÜGGE, Diss. Göttingen, (1879), p. 15; cf. also: K. WALLIN and P. KLASON, Ber. d. d. Chem. Ges. **12**, 1851. (1879). The crystals were obtained from alcohol or water. On the binary melting point-curve of *o*- and *p*-toluenesulphonamide, cf. P. V. MC. KIE, Journ. Chem. Soc. London, **113**, 799. (1918).

Fig. 2. *p*-Toluene-sulpho-methylamide.

Rhombic-bipyramidal.

$$a : b : c = 1,0358 : 1 : 2,6074.$$

The crystals represent evidently pseudo-tetragonal limiting forms; also optically they approach to tetragonal symmetry.

Observed Forms: $c = \{001\}$, very lustrous, predominant, giving splendid reflexes; $r = \{101\}$, and $q = \{011\}$, almost equally broad, well reflecting; $o = \{121\}$, small, dull, and difficult to measure accurately. The aspect of the crystals is thin tabular parallel to $\{001\}$, often with a slight elongation in the direction of the b -axis.

Angular values: Observed: Calculated:

$c : r = (001) : (101) = *$	68°20'	—
$c : q = (001) : (011) = *$	69 1	—
$r : r = (101) : (10\bar{1}) =$	43 20	43°20'
$q : q = (011) : (01\bar{1}) =$	41 58	41 58
$c : o = (001) : (121) =$	80 25	80 12
$o : o = (121) : (12\bar{1}) =$	18 10	18 36

Cleavage parallel to $\{001\}$.

The plane of the optical axes is $\{100\}$, c being 1st bisector. The apparent axial angle is very small, the crystals approaching also in this respect to uniaxiality.

The specific gravity of the crystals at room-temperature was: $d_{40} = 1,340$; the molecular volume is therefore: 138,06, and the topical parameters become: $\chi : \psi : \omega = 3,8442 : 3,7113 : 9,6770$.

§ 5. III. Nitro-*p*-Toluenesulpho-methyl-amide.

This compound is derived from the first by substitution of a hydrogen-atom of the NH_2 -group by CH_3 . From ethylacetate the substance crystallizes in beautiful, pale yellow prisms, and melts at 91° C. The crystals are generally dull and not easily measurable.

Monoclinic-prismatic.

$$a : b : c = 1,0522 : 1 : 0,3948;$$

$$\beta = 86^\circ 40\frac{1}{2}.$$

Forms Observed: $m = \{110\}$, the largest developed of all forms; $a = \{100\}$, narrow, and $r = \{101\}$ yet smaller; $o = \{111\}$, small, but yielding good reflexes.

The aspect of the crystals is that of long needles or prisms parallel to the c -axis.

Angular Values: Observed: Calculated:

$m : a = (110) : (100) = *$	46°24½'	—
$o : o = (111) : (1\bar{1}\bar{1}) = *$	71 52	—
$m : o = (\bar{1}10) : (111) = *$	78 18	—
$m : o = (110) : (111) =$	49 35	49°39½'
$m : m = (110) : (1\bar{1}0) =$	87 11	87 11
$c : m = (001) : (110) =$	—	87 42½'
$r : o = (101) : (111) =$	35 58	35 56

Perfectly cleavable parallel to $\{101\}$.

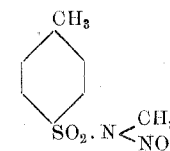
As the crystals were in every case dull and curvi-planed, more exact measurements appeared almost illusory.

The extinction on a was normally, on m obliquely orientated with respect to the edge $a : m$.

The specific weight of the crystals was: 1,485 at 16° C.; the equivalent-volume is, therefore: 154,21, and the topical axes are calculated at: $\chi : \psi : \omega = 7,5664 : 7,1910 : 2,8390$.

§ 6. IV. *p*-Toluene-sulpho-methylnitramide.

This compound, which possesses the structure:

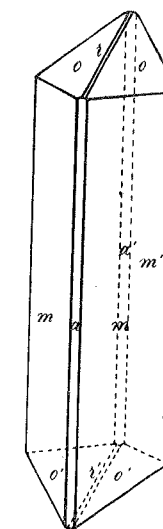


and melts at 60° C., crystallizes from a mixture of ligroin and ether in almost colourless flat needles, or in thick, short prisms. They are well built and give good reflexes.

Monoclinic-prismatic.

$$a : b : c = 1,3210 : 1 : 0,6892;$$

$$\beta = 78^\circ 6'.$$

Fig. 4. *p*-Toluene-sulpho-ethylnitramide.Fig. 3. Nitro-*p*-toluene-sulpho-methyl amide.

Forms Observed: $q = \{011\}$, large and very lustrous; $a = \{100\}$, large, mostly with one rudimentary face, but yielding good reflexes; $b = \{010\}$, narrower, sometimes curved; $r = \{101\}$, great and lustrous; $m = \{110\}$, perfectly reflecting; $\omega = \{111\}$, mostly narrow, but in the needle-shaped individuals as large as m , while r is here lacking in most cases; finally $o = \{311\}$, often well developed. The aspect of the crystals is thick prismatic, with a slight elongation parallel to the a -axis; rarely needles parallel to the same axis.

Angular values: Observed: Calculated:

$q : q = (011) : (0\bar{1}1) = *$	$67^{\circ}59\frac{1}{2}'$	—
$q : a = (011) : (100) = *$	$80\ 9$	—
$a : m = (100) : (110) = *$	$52\ 14\frac{1}{2}$	—
$q : b = (011) : (010) =$	$56\ 0$	$56^{\circ}\ 0'$
$a : r = (100) : (101) =$	$53\ 14$	$53\ 21$
$q : r = (011) : (101) =$	$41\ 14$	$41\ 9$
$b : m = (010) : (110) =$	$37\ 44$	$37\ 45\frac{1}{2}$
$a : w = (100) : (\bar{1}11) =$	$74\ 49$	$75\ 2$
$w : q = (\bar{1}11) : (011) =$	$25\ 1$	$24\ 49$
$a : o = (100) : (\bar{3}11) =$	$40\ 50$	$40\ 58$
$o : q = (\bar{3}11) : (011) =$	$59\ 1$	$58\ 53$

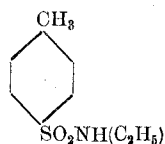
No distinct cleavage was found.

The extinction-angle on $\{010\}$ is 31° with respect to the a -axis.

The specific weight of the crystals is: 1,454 at room-temperature; the equivalent-volume is thus: 165,06, and the topical axes are calculated at: $\chi : \psi : \omega = 7,5309 : 5,7009 : 3,9291$.

§ 7. V. *p*-Toluene-sulpho-ethylamide.

This compound, which melts at 64° C., has the structure:



It crystallizes from a mixture of absolute alcohol and ether in colourless, parallelogram-shaped, thin plates, or small prismatic crystals. The solutions have a tendency to supersaturation.

Triclinic-pedial

$$a : b : c = 0,6481 : 1 : 0,4136;$$

$$\alpha = 77^{\circ}39\frac{1}{2}'; \quad A = 77^{\circ}37\frac{1}{2}'$$

$$\beta = 88^{\circ}6'; \quad B = 88^{\circ}21\frac{1}{2}'$$

$$\gamma = 102^{\circ}55\frac{1}{2}'; \quad C = 102^{\circ}53\frac{1}{2}'$$

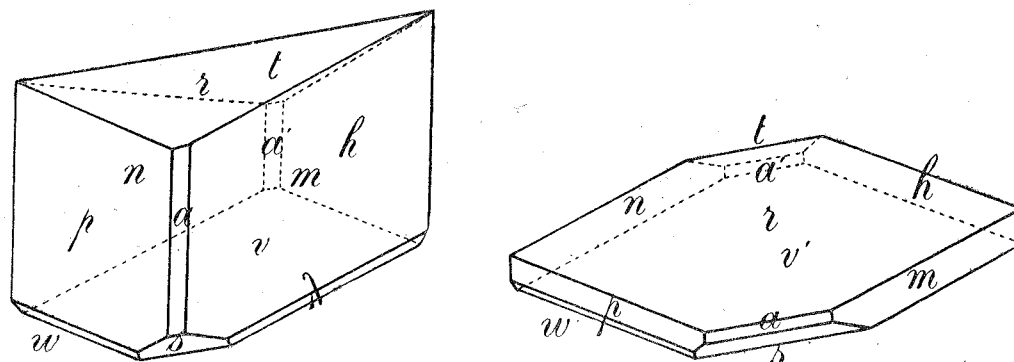


Fig. 5. *p*-Toluene-sulpho-ethylamide.

Forms observed: $r = \{101\}$ and $v = \{10\bar{1}\}$, large and very lustrous, mostly predominant, the crystals therefore being often tabular parallel to these planes; $t = \{10\bar{1}\}$, also lustrous, somewhat smaller than r and v ; $s = \{10\bar{1}\}$, smaller than t , and showing commonly a fine striation parallel to the edge $s : v$; $a = \{100\}$ and $a' = \{100\}$, narrow, but well reflecting; $m = \{110\}$, large, always showing a striation parallel to the edge $m : r$; $p = \{\bar{1}10\}$, $n = \{\bar{1}\bar{1}0\}$, and $h = \{\bar{1}10\}$, large and highly lustrous; $\omega = \{1\bar{2}1\}$ and $\lambda = \{12\bar{1}\}$, very narrow and badly reflecting, λ generally striated parallel to $m : v$; probably again $q = \{011\}$, very small and commonly not measurable. The aspect of the crystals is tabular parallel to r , or thick prismatic towards the c -axis. A cleavage occurs parallel to $\{101\}$.

Angular Values: Observed: Calculated:

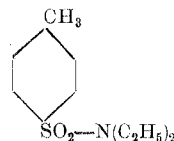
$a : r = (100) : (101) = *$	$58^{\circ}34'$	—
$a : s = (100) : (10\bar{1}) = *$	$56\ 14$	—
$a : p = (100) : (\bar{1}\bar{1}0) = *$	$37\ 11$	—
$a : m = (100) : (110) = *$	$29\ 23$	—
$r : p = (101) : (\bar{1}\bar{1}0) = *$	$58\ 17$	—
$r : t = (101) : (\bar{1}01) =$	$65\ 18$	$65^{\circ}12'$
$s : v = (10\bar{1}) : (\bar{1}0\bar{1}) =$	$65\ 10$	$65\ 12$
$s : p = (10\bar{1}) : (\bar{1}\bar{1}0) =$	$70\ 40$	$70\ 24$
$s : m = (10\bar{1}) : (110) =$	$56\ 39$	$56\ 37$
$r : m = (101) : (110) =$	$68\ 24$	$68\ 35\frac{1}{2}$
$w : p^2 = (\bar{1}2\bar{1}) : (\bar{1}\bar{1}0) =$	$51\ 2$	$51\ 13$

On all faces the optical extinction occurs obliquely with respect to the borders: on r about 46° with respect to the edge $r : p$; on p about 36° , on a about 43° , on m about 34° with respect to the direction of the c -axis. On r and p is the emergence of an optical axis observable, excentrically in the field of the microscope.

The specific gravity of the crystals is 1,307; the equivalent-volume therefore: 152,26, and the topical parameters become: $\chi : \psi : \omega = 4,6805 : 8,4202 : 3,4825$.

§ 8. VI. *p*-Toluene-sulpho-diethylamide.

This compound having the structure:



and melting at 59° C., crystallizes from a mixture of absolute alcohol and ethylacetate in the shape of thin, colourless, hexagonally bordered little plates, or in somewhat thicker tabular, and often opaque crystals.

Monoclinic-prismatic.

$$a : b : c = 1,0149 : 1 : 0,6762 ;$$

$$\beta = 72^{\circ}1'.$$

Observed Forms: $a = \{100\}$, predominant and very lustrous; $o = \{111\}$, $q = \{011\}$, $m = \{110\}$, $p = \{120\}$, all about equally broad and yielding splendid reflexes; $r = \{101\}$, very lustrous, well developed; $\omega = \{111\}$, somewhat narrower than o , but yielding also sharp images; $n = \{210\}$, and $b = \{010\}$, extremely narrow, often absent and giving feeble reflexes. The crystals are well built, and allow exact measurements. Their aspect is tabular parallel to a and elongated in the direction of the c -axis. The crystals are very brittle.

Angular values:	Observed:	Calculated:
$a : o = (100) : (111) = *$	49°40'	—
$a : q = (100) : (011) = *$	74 57	—
$a : r = (100) : (101) = *$	44 17½	—
$o : q = (111) : (011) =$	25 17	25°17'
$q : \omega = (011) : (\bar{1}11) =$	32 18	32 20½
$\omega : a = (\bar{1}11) : (\bar{1}00) =$	72 45	72 42½
$o : r = (111) : (101) =$	25 15	25 17
$b : o = (010) : (111) =$	64 45	64 43
$a : m = (100) : (110) =$	43 58½	43 59½
$m : p = (110) : (120) =$	18 34	18 32½

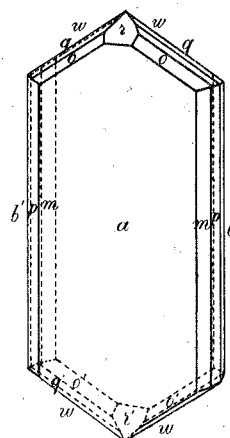


Fig. 6. *p*-Toluene-sulpho-diethylamide.

Angular values:	Observed:	Calculated:
$p : b = (120) : (010) =$	27 23	27 23
$b : m = (010) : (110) =$	46 2	46 0½
$a : n = (100) : (210) =$	26 9	25 46
$n : m = (210) : (110) =$	17 59	18 13½
$a : p = (100) : (120) =$	62 31	62 37

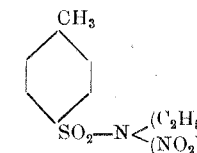
No distinct cleavage was found.

The optical axial plane is $\{010\}$. Very strong, inclined dispersion, with $\rho < \nu$; on $\{100\}$ one axis emerges excentrically in the field of the microscope.

The specific weight of the crystals at 15° C. was: 1,230; the equivalent-volume is therefore: 184,55, and the topical parameters are calculated to: $\chi : \psi : \omega = 6,6611 : 6,5633 : 4,4381$.

§ 9. VII. *p*-Toluene-sulpho-ethylnitramide.

This substance, which has the configuration:



crystallizes from ether in big, colourless crystals, or in hexagonally-shaped tables. It melts at 69° C.

Monoclinic-prismatic.

$$a : b : c = 1,0178 : 1 : 1,1005 ;$$

$$\beta = 88^{\circ}11'.$$

Forms Observed: $c = \{001\}$, strongly predominant and lustrous; $a = \{100\}$, sometimes large, often also narrower, but always yielding sharp reflexes; $m = \{130\}$, well developed, but often with curved faces and somewhat dull; $r = \{203\}$, well reflecting, often absent; $\omega = \{133\}$, extremely narrow, in most cases absent, and only approximately measurable. The aspect of the crystals is either short prismatic with an elongation parallel to the b -axis, or thin lamellar parallel to $\{001\}$.

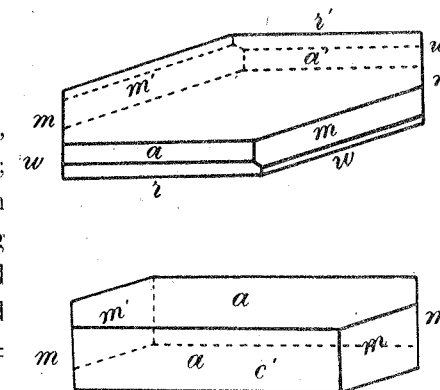


Fig. 7. *p*-Toluene-sulpho-ethylnitramide.

Angular Values:	Observed:	Calculated:
$a : c = (100) : (001) = *$	88°11'	—
$a : m = (100) : (130) = *$	71 51½	—
$a : r = (100) : (20\bar{3}) = *$	55 25	—
$c : r = (001) : (20\bar{3}) =$	36 24	36 24
$m : m = (130) : (1\bar{3}0) =$	36 27	36 17
$c : w = (001) : (\bar{1}33) =$	50 8	49 29
$m : w = (\bar{1}30) : (133) =$	40 58	41 5
$c : m = (001) : (130) =$	89 24	89 26

Very perfectly cleavable parallel to {001}.

On a and c the extinction is normally orientated, but often of undulatory character, as the result of geometrical anomalies in the structure of the crystals.

The specific gravity of the crystals was 1,450; the equivalent-volume is therefore: 168,27, and the topical parameters become: $\chi : \psi : \omega = 5,4115 : 5,3169 : 5,8513$.

§ 10. VIII. Nitro-p-Toluene-sulpho-ethyl-nitramide.

This substance, which melts at 76° C., can only rarely be obtained in measurable crystals. Those here investigated were deposited from a hot saturated solution in carbon tetrachloride by very slow evaporation.

Thin, yellow, very lustrous and transparent plates, commonly with hemimorphic development (fig. 8).

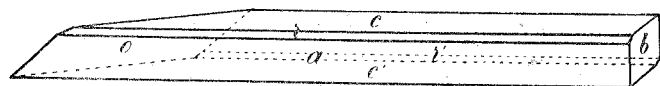


Fig. 8. Nitro-p-Toluene-sulpho-ethyl-nitramide.

Monoclinic, probably sphenoidal.

$$a : b : c = 0,4812 : 1 : 0,8766 ;$$

$$\beta = 85^{\circ}5'.$$

Forms Observed: $c = \{001\}$, predominant, and very lustrous, $o = \{\bar{1}\bar{1}1\}$, yielding ideal reflexes, often with only a single plane; $a = \{100\}$, giving good mirror-images; $b = \{010\}$, often absent, but otherwise well reflecting; $r = \{70\bar{5}\}$, very narrow, often totally absent. The crystals often show oscillatory angular values, principally in the zone of the orthodiagonal, and multiple reflexes. The aspect is tabular parallel to {001}, and strongly elongated towards the b -axis.

Angular values:	Observed:	Calculated:
$c : a = (001) : (100) = *$	85° 5'	—
$c : o = (001) : (\bar{1}\bar{1}1) = *$	67 16	—
$a : o = (\bar{1}00) : (\bar{1}\bar{1}1) = *$	37 21	—
$c : r = (001) : (705) =$	64 42	64°23'
$r : a = (705) : (100) =$	20 16	20 42
$c : b = (001) : (010) =$	89 52	90 0
$o : r = (\bar{1}\bar{1}1) : (705) =$	54 23	54 24

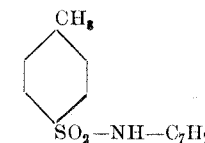
No distinct cleavage was found.

The optical axial plane is parallel to {010}; on c and a both an optical axis emerges excentrically.

The specific weight of the crystals is: 1,555; the equivalent-volume therefore: 156,91, and the topical parameters are calculated at: $\chi : \psi : \omega = 3,4652 : 7,2001 : 6,3119$.

§ 11. IX. p-Toluene-sulpho-benzylamide.

Structure:



From a mixture of ether and alcohol the compound crystallizes in large, colourless crystals with varying aspect. It melts at 113° C. The crystals are well built and allow exact measurements.

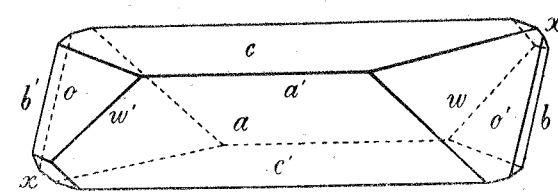


Fig. 9. p-Toluene-sulpho-benzylamide.

Triclinic-pinacoidal.

$$a : b : c = 0,9778 : 1 : 0,8991.$$

$$A = 83^{\circ}32' \quad . \quad a = 83^{\circ}24\frac{1}{2}'.$$

$$B = 90^{\circ}56' \quad . \quad \beta = 91^{\circ}33'.$$

$$C = 95^{\circ}15' \quad . \quad \gamma = 95^{\circ}96'.$$

Forms Observed: $a = \{100\}$, and $c = \{001\}$, large and very lustrous; in most cases a is somewhat larger than c ; $\omega = \{111\}$ and $o = \{\bar{1}\bar{1}1\}$,

large, lustrous, and about equally well developed; $b = \{010\}$, narrow, somewhat dull, commonly with only a single face, often totally absent; $x = \{1\bar{1}\bar{1}\}$, small, dull, but well measurable. The aspect of the crystals is ordinarily prismatic parallel the b -axis.

Angular values:	Observed:	Calculated:
$a : c = (100) : (001) = *$	89° 4'	—
$c : o = (001) : (\bar{1}\bar{1}\bar{1}) = *$	47 33	—
$c : w = (001) : (111) = *$	55 47	—
$a : o = (100) : (\bar{1}\bar{1}\bar{1}) = *$	59 4	—
$a : w = (\bar{1}00) : (111) = *$	51 12½'	—
$o : w = (\bar{1}\bar{1}\bar{1}) : (111) =$	66 45½'	66°50½'
$o : b = (\bar{1}\bar{1}\bar{1}) : (0\bar{1}0) =$	55 38½'	55 46
$b : w = (0\bar{1}0) : (111) =$	57 33½'	57 23½'
$x : a = (\bar{1}\bar{1}\bar{1}) : (100) =$	57 38	57 38
$b : x = (0\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	62 50	62 42½'
$o : x = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	77 52	77 53
$x : c = (\bar{1}\bar{1}\bar{1}) : (001) =$	54 24½'	54 34

No distinct cleavability was observed.

The extinction on a and c was oblique with respect to the edge $a : c$.

The specific weight of the crystals was: 1,313 at 17° C.; the equivalent-volume is thus: 198,78, and the topical parameters become: $\chi : \psi : \omega = 5,9793 : 6,1150 : 5,4981$.

§ 12. X. Nitro-*p*-Toluene-sulpho-benzyl-nitramide.

This compound, melting at 153° C., crystallizes from ethylacetate in small, very lustrous, colourless crystals. They often show somewhat oscillatory angular values; the faces of $\{001\}$ are, moreover, often curved. Exact measurements were, however, possible.

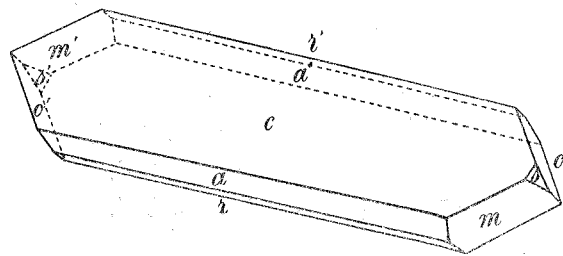


Fig. 10. Nitro-*p*-Toluene-sulpho-benzyl-nitramide.

Triclinic-pinacoidal.

$$a : b : c = 1,8095 : 1 : 1,3139.$$

$$A = 95^{\circ}34' \quad \alpha = 100^{\circ}50'$$

$$B = 101^{\circ}22' \quad \beta = 104^{\circ}43'$$

$$C = 67^{\circ}20' \quad \gamma = 65^{\circ}33'.$$

Forms Observed: $c = \{001\}$, large and lustrous, sometimes a little curved; $a = \{100\}$, narrower, but very lustrous; $m = \{110\}$ and $o = \{111\}$, almost equally well developed, and yielding good reflexes; $s = \{011\}$, small, but well measurable; this form is often absent. Further sometimes again: $r = \{\bar{1}01\}$, very narrow. The aspect of the crystals is tabular, thin plates parallel to c , and often elongated in the direction of the b -axis.

Angular values:	Observed:	Calculated:
$a : c = (100) : (001) = *$	78°38'	—
$c : o = (001) : (\bar{1}\bar{1}\bar{1}) = *$	62 28½'	—
$a : m = (100) : (110) = *$	79 13	—
$c : m = (001) : (110) = *$	77 25	—
$o : m = (\bar{1}\bar{1}\bar{1}) : (110) = *$	54 10½'	—
$a : o = (\bar{1}00) : (\bar{1}\bar{1}\bar{1}) =$	56 48½'	56°47'
$o : s = (\bar{1}\bar{1}\bar{1}) : (0\bar{1}\bar{1}) =$	44 19½'	44 10
$s : a = (0\bar{1}\bar{1}) : (100) =$	79 3	79 1¾'
$a : r = (\bar{1}00) : (\bar{1}01) =$	59 16	59 7
$r : c = (\bar{1}01) : (001) =$	42 6	42 15
$s : c = (011) : (001) =$	—	50 52

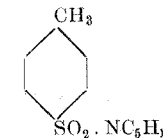
No distinct cleavage was observed.

On $\{001\}$ the extinction-angle is 8° with respect to the edge $a : c$. In convergent polarized light one hyperbola is visible at the border of the field.

The specific gravity of the crystals is: 1,530 at 17° C.; the equivalent-volume is therefore: 229,54, and the topical parameters are calculated at: $\chi : \psi : \omega = 8,6739 : 4,7934 : 6,2983$.

§ 13. XI. *p*-Toluene-sulpho-piperidide.

Structure:



This substance, which melts at 98° C., was obtained from ether in the form of large, flat, colourless, very lustrous crystals of rec-

tangular shape. They are well built, beautifully translucent, and allow very accurate measurements.

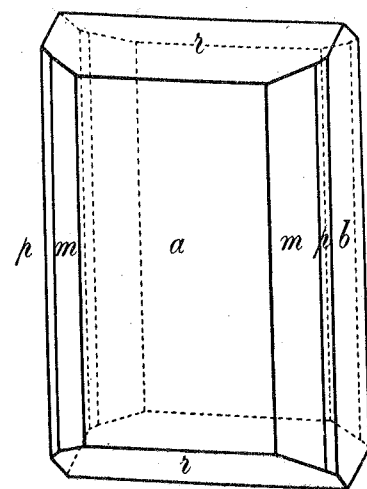


Fig. 11. *p*-Toluene-sulpho-piperidide.
Rhombic-bipyramidal
 $a : b : c = 0,7474 : 1 : 0,3790$.

Forms Observed: $a = \{100\}$, predominant and yielding good reflexes; $m = \{110\}$ and $b = \{010\}$, large and very lustrous; $p = \{120\}$, very narrow; $r = \{101\}$, large and giving good reflexes.

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) = *$	$36^{\circ}46\frac{1}{2}'$	—
$a : r = (100) : (101) = *$	$63^{\circ}6\frac{1}{2}'$	—
$m : p = (110) : (120) =$	$19^{\circ}23\frac{1}{2}'$	$19^{\circ}26\frac{1}{2}'$
$p : b = (120) : (010) =$	$33^{\circ}50'$	$33^{\circ}47'$
$r : r = (101) : (\bar{1}01) =$	$53^{\circ}46\frac{1}{2}'$	$53^{\circ}46\frac{2}{3}'$

No distinct cleavage was found.

The optical axial plane is $\{001\}$, with the b -axis as first bisector; the dispersion, of rhombic character, is very appreciable: $\sigma < \nu$. The apparent axial angle is only small.

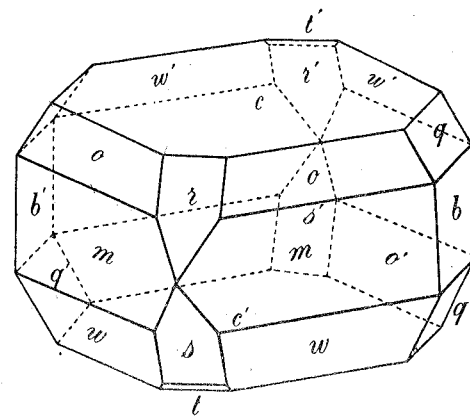
The specific weight of the crystals is: 1,281 at 15° C.; the equivalent-volume therefore: 186,57, and the topical axes become: $\chi : \psi : \omega = 6,5029 : 8,7005 : 3,2967$.

§ 14. XII. Nitro-*p*-Toluene-sulpho-piperidide.

The substance melts at 108° C., and crystallizes from ethylacetate in splendid large, somewhat pale yellowish, translucent, very lustrous crystals. They are well built, and allow good measurements.

Monoclinic-prismatic.
 $a : b : c = 0,7466 : 1 : 1,5713$.
 $\beta = 78^{\circ}39'$.

Forms observed: $c = \{001\}$, predominant; $m = \{110\}$, large and lustrous, shows sometimes a fine striation parallel to the edges $m : c$; $o = \{111\}$, and $\omega = \{1\bar{1}1\}$, about equally large, but a little bit narrower than m ; $r = \{101\}$, well reflecting;



$s = \{\bar{1}01\}$, somewhat smaller than r , often absent; $t = \{hok\}$, extremely narrow and not measurable only rarely present; $b = \{010\}$, small and narrow, dull; $q = \{011\}$ clearly developed, yielding good reflexes. The aspect is often isometrical, or somewhat flattened parallel to $\{001\}$.

Angular Values:	Observed:	Calculated:
$c : \omega = (001) : (\bar{1}11) = *$	$77^{\circ}11'$	—
$\omega : \omega = (\bar{1}11) : (\bar{1}\bar{1}1) = *$	$71^{\circ}22\frac{1}{2}'$	—
$m : c = (110) : (001) = *$	$80^{\circ}52'$	—
$c : r = (001) : (101) =$	$55^{\circ}28'$	$55^{\circ}34\frac{2}{3}'$
$r : s = (101) : (10\bar{1}) =$	$50^{\circ}13\frac{1}{2}'$	$50^{\circ}16\frac{1}{3}'$
$s : c = (\bar{1}01) : (001) =$	$74^{\circ}11'$	$74^{\circ}9'$
$c : q = (001) : (011) =$	$56^{\circ}57'$	$57^{\circ}0\frac{2}{3}'$
$b : q = (010) : (011) =$	$33^{\circ}3'$	$32^{\circ}59\frac{1}{3}'$
$\omega : s = (\bar{1}11) : (\bar{1}01) =$	$35^{\circ}41'$	$35^{\circ}41\frac{1}{4}'$
$m : m = (110) : (\bar{1}\bar{1}0) =$	$72^{\circ}22'$	$72^{\circ}24\frac{1}{2}'$
$c : o = (001) : (111) =$	$61^{\circ}20'$	$61^{\circ}13\frac{1}{2}'$
$o : m = (111) : (110) =$	$19^{\circ}30'$	$19^{\circ}8'$
$m : \omega = (110) : (1\bar{1}\bar{1}) =$	$21^{\circ}57\frac{1}{2}'$	$21^{\circ}57'$
$m : b = (110) : (010) =$	$53^{\circ}49'$	$53^{\circ}47\frac{3}{4}'$

Very perfectly cleavable parallel to $\{001\}$, distinctly parallel to $\{110\}$. On $\{001\}$ diagonal extinction.

The specific weight of the crystals at 15° C. was: 1,384; the equivalent-volume is therefore: 205,20, and the topical parameters become: $\chi : \psi : \omega = 4,2031 : 5,6259 : 8,8455$.

Survey of the Crystallogonomical Relations between the Derivatives of p-Toluene-sulpho-amide here investigated.

Name of the Compound:	Melting-point:	Symmetry:	Axial ratio:	Spec. Volume:	Topical parameters:
p-Toluene-sulpho-amide	137° 5 C.	Mon. prism.	1,2016 : 1 : 0,9364 $\beta = 87^{\circ}29'$	133,99	5,5537 : 4,5194 : 5,3383
Nitro-p-toluene-sulpho-amide	141°	Mon. prism. (pseu. o-rhomb.)	1, 2289 : 1 : 1,1812 $\beta = 90^{\circ}$	138,06	3,8442 : 3,7113 : 9,6770
p-Toluene-sulpho-methylamide	76°	Rhomb. bipyrr.	1,0358 : 1 : 2,6074	154,21	7,5664 : 7,1910 : 2,8390
Nitro-p-toluene-sulpho-methylamide	91°	Mon. prism.	1,0522 : 1 : 0,3948 $\beta = 86^{\circ}40\frac{1}{2}'$	165,06	7,5309 : 5,7009 : 3,9291
p-Toluene-sulpho-methylnitramide	60°	Mon. prism.	1,3210 : 1 : 0,6892 $\beta = 78^{\circ}6'$	152,26	4,6805 : 8,4202 : 3,4825
p-Toluene-sulpho-ethylamide	64°	Tricl. (pediaal)	0,6481 : 1 : 0,4136 $\alpha = 77^{\circ}39'$; $\beta = 88^{\circ}6'$; $\gamma = 102^{\circ}55'$	184,55	6,6611 : 6,5633 : 4,4381
p-Toluene-sulpho-diethylamide	59°	Mon. prism.	1,0149 : 1 : 0,6762 $\beta = 72^{\circ}1'$	168,27	5,4115 : 5,3169 : 5,8513
p-Toluene-sulpho-ethylnitramide	69°	Mon. prism.	1,0178 : 1 : 1,1005 $\beta = 88^{\circ}11'$	156,91	3,4652 : 7,2001 : 6,3119
Nitro-p-Toluene-sulpho-ethylnitramide	76°	Mon. (sfenoid.)	0,4812 : 1 : 0,8766 $\beta = 85^{\circ}5'$	198,78	5,9793 : 6,1150 : 5,4981
p-Toluene-sulpho-benzylamide	113°	Tricl. pinac.	0,9778 : 1 : 0,8991 $\alpha = 83^{\circ}24\frac{1}{2}'$; $\beta = 91^{\circ}33'$; $\gamma = 95^{\circ}26'$	229,54	8,6739 : 4,7934 : 6,2983
Nitro-p-toluene-sulpho-benzylnitramide	153°	Tricl. pinac.	1,8095 : 1 : 1,3139 $\alpha = 100^{\circ}50'$; $\beta = 104^{\circ}43'$; $\gamma = 65^{\circ}33'$	186,57	6,5029 : 8,7005 : 3,2976
p-Toluene-sulpho-piperidide	98°	Rhomb. bipyrr.	0,7474 : 1 : 0,3790	205,20	4,2031 : 5,6295 : 8,8455
Nitro-p-toluene-sulpho-piperidide	108°	Mon. prism.	0,7466 : 1 : 1,5713 $\beta = 78^{\circ}39'$		

Groningen, June 1920.

Laboratory for Inorganic and Physical
Chemistry of the University.

Zoology. "The colour-markings on the body of Lepidoptera, compared to those of their larvae and pupae, and to those of their wings". By Prof. J. F. VAN BEMMELLEN.

(Communicated at the meeting of January 31, 1920).

In former communications I have expressed my conviction, that originally an intimate connection must have existed between the colour-markings of caterpillar, pupa and butterfly of the same species, all three being only varieties of one and the same archaic form. Consequently the few cases, in which this connection is evident at first sight, should not be considered as mere casualities, but as resulting from the preservation of the primitive condition. SCHIERBEEK, who chiefly studied the setal pattern of the youngest instars of caterpillars, but also gave his attention to the colour-markings of a few older caterpillars, and to pupae, has fully corroborated my views. DE MEYERE on the contrary, in his paper: Zur Zeichnung des Insecten-im besondern des Dipteren- und Lepidopterenflügels, 1916, has expressed his doubts about them, where he says on p. 131: "In my opinion the striking difference between the pupal- and the imaginal markings precisely shows that they have had an independent origin, and have followed different ways: — just as we found it in nearly related Diptera, we here see it in different stages of the same animal".

And further on:

"According to my view the colour-markings of the pupa of diurnal Lepidoptera are as much of recent origin as their frequently grotesque shape and their very varying mode of fixation. The same might apply to pupal markings in comparison to those of caterpillars".

In his second paper: Zur Evolution der Zeichnung bei den holo-metabolen Insecten, he writes on p. 70:

"I consider the striking colour-markings of many butterfly-pupae as a secondary feature in these organisms, exposed to light as they are. In a similar manner the pupa of *Abraaxas grossulariata*, which settles unhidden in shrubs, shows special coloration. VAN BEMMELLEN's assertion, that this Geometrid should show a primitive coloration in all instars, does not seem right to me, at least in regard to the pupa The pupa of *Abr. sylvata*, which hibernates in the earth, is quite dark; without doubt in this case, the older condition. The real primitive condition I believe to occur in the light-brown