

*Citation:*

F.M.Jaeger, On the question as the miscibility and the formanalogy in aromatic Nitro-and Nitroso-compounds., in:

KNAW, Proceedings, 10 II, 1907-1908, Amsterdam, 1908, pp. 436-440

usage, to denote also in Dutch the *krystalline Schiefer* by means of the term *schist* (pl. *schisten*) borrowed from the Greek, and to confine one's self in the application of the derived-adjective *schisteus* and the substantive *schistositeit* exclusively to this class of metamorphosed rocks.

While, in conclusion, I express my special gratitude to Prof. J. W. MULLER for his kindly furnished contributions and for some valuable hints, I cannot omit tendering my best thanks to Prof. A. WICHMANN and Prof G. A. F. MOLENGRAAFF for their lively interest and the support with which they obliged me.

**Chemistry.** — “On the question as to the miscibility and the form-analogy in aromatic Nitro- and Nitroso-compounds”. By Dr. F. M. JAEGER. (Communicated by Prof. A. P. N. FRANCHIMONT).

1. The following communication contains a further contribution to the knowledge of the mutual behaviour of the aromatic nitro- and nitroso-derivatives, of which several particulars were given previously. The entire miscibility in the solid condition, and the form-analogy bordering on isomorphism, were established in the case of *p*-Nitro- and *p*-Nitrosodiethylaniline<sup>1)</sup>, while afterwards, in a more extended paper of a more general nature<sup>2)</sup>, the mutual comparison of *p*-Nitro- and *p*-Nitrosophenol and of *o*-Nitroso- and *o*-Dinitrobenzene was discussed. It then appeared that no *general* rule could be laid down as to the connection of the two classes of compounds.

A new pair of similar comparable substances which are interesting from more than *one* point of view, namely *o*-Nitro- and *o*-Nitrosoacetanilide were now studied. The result was different from that obtained with *p*-Nitro- and *p*-Nitrosodiethylaniline although analogy is present in *one* of the axial relations, and a solid solution of the two components appears to be possible to some slight extent.

§ 2. **Ortho-Nitro-Aceto-Anilide.**

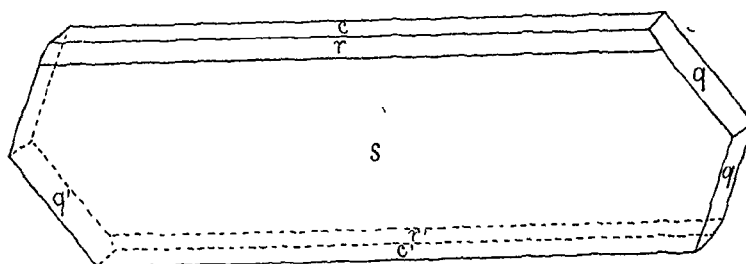
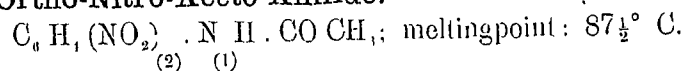


Fig. 1.

<sup>1)</sup> F. M. JAEGER, These Proc. VII, p. 660,

<sup>2)</sup> idem, Ueber Mischbarkeit von festen Phasen, Z. f. Kryst. 42, 236—276 (1906).

On account of its great solubility in most solvents it is very difficult to obtain this compound in a properly crystallised form. The greatest success is met with by very slow evaporation of its solution in dilute alcohol when it crystallises in pale yellow, very thin laminae with extended hexagonal periphery; the crystals are very transparent and give sharp signal-images.

The symmetry is *monoclinic-prismatic*. In the choice of the plane-symbols adopted here the axial relation is calculated on:

$$a : b : c = 0,8935 : 1 : 1,9198$$

$$\beta = 83^{\circ}51'$$

Forms observed:  $s = \{101\}$ , strongly predominant and yielding sharp reflexes;  $r = \{101\}$  much narrower, but gives a good reflection;  $c = \{001\}$ , narrower than  $r$ ;  $q = \{011\}$ , also narrow, but reflects well. The habit is flattened along  $\{\bar{1}01\}$  with considerable elongation along the  $b$ -axis.

The following angular values were determined:

	<i>Measured:</i>	<i>Calculated:</i>
$c : q = (001) : (011) =$	$* 62^{\circ}21'$	—
$q : s = (011) : (10\bar{1}) =$	$* 80^{\circ}57'$	—
$c : r = (001) : (101) =$	$* 60^{\circ} 4'$	—
$r : s = (101) : (10\bar{1}) =$	$49^{\circ}45'$	$49^{\circ}45'$
$s : c = (10\bar{1}) : (00\bar{1}) =$	$70^{\circ}11'$	$70^{\circ}11'$

A distinct plane of cleavage was not found.

In the orthodiagonal zone the direction of extinction is orientated everywhere perpendicular to the direction of the  $b$ -axis. On  $\{\bar{1}01\}$  no perceptible dichroism is observable.

The optical properties of the substance in convergent polarised light are very remarkable.

For the red, yellow and most of the green rays of the spectrum the axial plane =  $\{010\}$ ; extraordinarily strong, inclined dispersion: the axial angle for the red is much larger than that for the green. The character of the double refraction is positive.

On the other hand, the axial angle for the blue and violet rays is situated perpendicular on  $\{010\}$  with a horizontal dispersion. The axial angle for all rays is but small.

The curious colourphenomena in white light exhibited by this substance, which thus possesses at the same time inclined and horizontal dispersion, lend themselves particularly well to the demonstration of anomalous dispersion in biaxial crystals.

The sp.gr. of the crystals is 1.419 at  $15^{\circ}$ ; the equivalent volume is therefore 126.85.

Topic parameters:  $\chi : \psi : \omega = 3,7578 : 4,2058 : 8,0744$ .

## § 3. Orthonitroso-Aceto-Anilide.

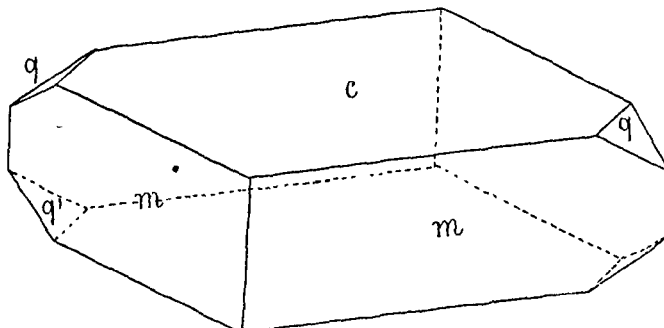


Fig. 2.

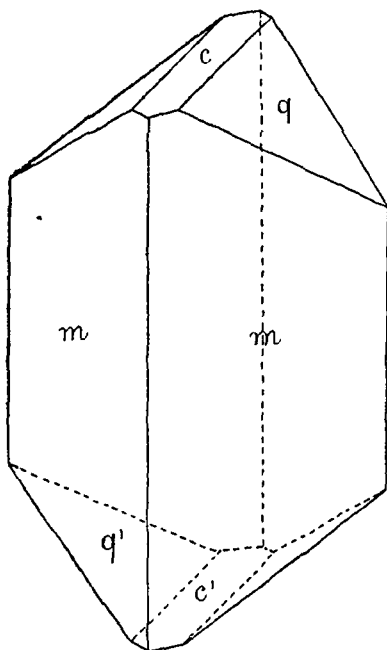


Fig. 3.

Through the kindness of Dr. F. LUCENS of *München*, who was the first to prepare this substance (Ber. 1907 40. 1083), I received a small quantity of the crystallised compound obtained by cooling the hot alcoholic solution. The crystals exhibited the habit of fig. 2; from a mixture of ether and benzene I obtained the thick prismatic crystals of fig. 3. The prism-planes, which often act as resting planes of the crystals in the mother liquor, were in consequence mostly curved and unsuitable for accurate measurement, whilst the forms *c* and *q* always gave ideal reflexes. The crystals have a brilliant emerald green colour and are quite transparent.

The symmetry is *monoclinic-prismatic*; the axial relation was calculated on:

$$a : b : c = 0,8940 : 1 : 0,7295$$

$$\beta = 82^\circ 6'$$

Forms observed:  $c = \{001\}$ , predominant in the crystals obtained from alcohol and always very shining;  $m = \{110\}$ , well developed but often with curved plane;  $q = \{011\}$ , giving ideal reflexes and mostly exhibiting rather large planes;  $a = \{100\}$ , exceedingly narrow and dim. The habit is flattened along *c* or long prismatic parallel

the  $c$ -axis, with flattening along two parallel planes of  $m$ ; perfectly cleavable towards  $\{001\}$ .

The following angles were measured:

	<i>Measured:</i>	<i>Calculated:</i>
$c : m = (001) : (110) =$	$84^{\circ} 5\frac{1}{4}'$	—
$c : q = (001) : (011) =$	$35^{\circ} 51'$	—
$m : m = (110) : (\bar{1}\bar{1}0) =$	$83^{\circ} 3'$	—
$m : q = (110) : (011) =$	$61^{\circ} 55\frac{1}{2}'$	$61^{\circ} 51\frac{1}{2}'$
$m : q = (110) : (011) =$	$72^{\circ} 18'$	$72^{\circ} 15'$
$m : a = (110) : (100) =$	$41^{\circ} 34'$	$41^{\circ} 31\frac{1}{2}'$

On  $\{001\}$  not observable but on  $\{110\}$  very distinctly dichroic; for vibrations parallel to the  $c$ -axis, grass-green; and yellowish-green for vibrations perpendicular thereon. The angle of extinction is very difficult to determine; it amounts to about  $12^{\circ}$  in regard to the  $c$ -axis on the planes of  $\{110\}$ .

The optical axial plane is  $\{010\}$ ; on  $\{001\}$  one axis is visible at a small angle with the normal to that plane; the inclined dispersion is extraordinarily strong:  $\rho < v$ .

The sp. gr. of the crystals is 1.351 at  $15^{\circ}$ , the equivalent volume is 121.39.

Topic parameters:  $\chi : \psi : \omega = 5.1206 : 5.7277 : 4.1784$ .

4. A small addition of the nitroso-compound to the nitro-compound causes a perceptible depression of the melting point of the latter substance. As, therefore, no certainty is obtained as to the formation of mixed crystals of these closely related derivatives — for a melting curve with an absolute minimum might be also present — a few preliminary quantitative experiments were carried out, which showed that we have here indeed an ordinary binary meltingpointline with eutecticum. It was further shown by more detailed microscopic tests that from mixed fusions of the two compounds is always deposited a *mixture* of the *yellow* nitroaceto-anilide crystals and the *green* nitrosoaceto-anilide crystals with a totally different aspect. At the side of the nitroso-compound a perceptible quantity of the nitro-derivative is carried down by the deposited crystals as solid solution; at the side of the nitro-derivative a formation of solid solutions could not be ascertained in this way. In any case, if there should be a slight mixing, it is limited on the side of the nitroso-compound to a few percent of the nitro-compound; the hiatus is therefore enormously extended.

Finally be it observed here that both substances are very volatile; the vapour of the nitroso-compound is *yellowish green*.

A few experiments were tried to sublime mixtures of the two compounds. The deposit on the concave coveringglass then consists of a network of dendritic, strongly pleochroic (colourless — yellowish-green) little crystals, between which are found the square-shaped crystals of the nitroso-compound, besides the yellow individuals of the nitro-compound, united in clusters.

The first mentioned crystals contain chiefly the nitroso-compound and probably to a very small amount also the nitro-compound, so this may be a new case of the formation of solid solutions by sublimation. Probably, this pair of compounds lends itself to the measuring of the vapour tensions of these solid solutions.

Zuandam, December 1907.

**Physics.** — “*Observation of the magnetic resolution of spectral lines by means of the method of FABRY and PEROT.*” By Prof. P. ZEEMAN.

The interference method of the parallel semi-silvered plates, worked out with so much ingenuity by FABRY and PEROT<sup>1)</sup> excels above all other spectroscopic modes of procedure by the accuracy with which its theoretical foundations may be practically realized.

The principal task of the experimenter in applying this method has become to effect the perfect parallelism of the reflecting silvered plates.

In order to test by an independent method some recent results obtained in an investigation of the magnetic resolution of spectral lines<sup>2)</sup> the method of FABRY and PEROT seemed most appropriate. Especially it appeared possible to extend at the same time the investigation to the behaviour of the lines in weak fields. The present paper is preliminary to a discussion of numerical results. I think it beforehand very improbable that errors of ruling of the ROWLAND grating will turn out to be the reason of the asymmetrical resolution of some lines, which I have described.

The method of FABRY and PEROT is applied in the present paper for the first time to an investigation of the magnetic separation of spectral lines. In some places in the literature of the subject the opinion is expressed that the method of interference fringes of silvered layers cannot be used for the subject under review. The

1) FABRY et PEROT, Ann. de Chimie et de Physique 1899—1904.

2) ZEEMAN, These Proceedings, November 1907.