

Citation:

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Chemistry. — “*On miscibility in the solid aggregate condition and isomorphy with carbon compounds.*” [First communication].
By Dr. F. M. JÄGGER. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

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

Since the discovery of isomorphy by MITSCHERLICH the power of isomorphous compounds to form, on being mixed, a homogeneous solid phase of gradually-varying composition has been experimentally demonstrated in numerous cases.

In recent years several investigators have started theories as to the course of the melting curves likely to be exhibited by such mixing-series, and in conjunction with the theory of the equilibrium of phases and with the aid of thermodynamical developments, a fairly clear idea has been formed of the special cases which may be expected to occur with substances of the said kind.

On the other hand, it is not permissible to draw conclusions as to existing isomorphy, *solely* on account of the course of the melting curve or the solubility lines. Since the introduction in chemistry of the idea of “solid solutions”, many cases have already been pointed out where amorphous or even crystallised solid solutions exist of substances which bear either *no* or an unknown crystallonomic relation to each other. We have only to think for instance of amorphous glasses and on the other hand of the crystalline mixtures of ferric-chloride and sal-ammoniac. The difficulty is felt in a particularly striking manner in the chemistry of the carbon compounds; not only do we know continuous series of crystalline mixtures between morphotropously allied carbon-containing derivatives, as in MUTHMANN’s terephthalic-acid derivatives, but such mixing even in the crystalline condition, has also been observed in the case of organic molecules which have little or nothing in common.

BRUNI and his collaborators, who have made a long series of cryoscopic determinations conclude that the most dissimilar organic substances may yield “mixed crystals” and “solid solutions” of whose crystallonomic relation not only nothing as a rule is known, but of which the crystallographer will think the chances of isomorphy but very small.

In any case the relation existing between “crystallonomic form-relation” and “miscibility” is as yet quite unknown. If substances are isomorphous, that is if crystalline phases possess regulated molecular structures, which may be assumed to be formed from each other by a slight deformation, such phases may jointly yield a homogeneous mixing-phase of variable composition and their relations

based on the equilibrium of phases will take the course indicated by theory. But the reverse is by no means the case and the question as to the existence of "isomorphy" can only be satisfactorily solved by a crystallonomic investigation.

The problem has a particular interest in so far as it relates to the determination of the limits in which morphotropously-related kinds of molecules may exhibit such a miscibility. For the word "isomorphy" relates to a number of special cases in a series of much more general phenomena of crystallonomy, namely, to those which show the relation between the chemical constitution of the substances which have substitution-relations, with their innate crystalline form, which phenomena are expressed by the name of morphotropy. If the chemical relation of such substitution derivatives is confined *within* certain limits such morphotropic substances may become "isomorphotropic" and will then be able to combine with each other in a limited or may be unlimited proportion. And if the relation of such substances has become so intense that a nearly identical property must be attributed to their crystal-structures on account of *all* their physical properties, such isomorphotropic substances actually become "isomorphous" and mixing is then always possible.

From the above it follows that the idea of "isomorphy" admits of a certain gradation; only the crystallonomer can determine in each case the degree of "isomorphy" by measuring the size indicated by the parameters of the molecular structure in the cases to be compared and particularly by studying the analogy in the cohesion-phenomena of the crystal-phase. As the differences in the values of the said molecular structure-parameters become smaller and a more complete similarity in the directions of cleavage and nature of surface of the similar limiting planes is found, a more complete isomorphy exists and the probability of a complete miscibility in the crystallised condition is at the same time enhanced.

It cannot be doubted that in the cases investigated by BRUNI there may be instances of such *real* isomorphy and the following research may even prove this fact. But it must also not be lost sight of that many cases of miscible substances supposed to be instances of "isomorphy" are only cases of isomorphotropy or even only of morphotropy within relatively large limits.

All this renders it highly desirable to undertake an exhaustive investigation of organic substances as to their miscibility in the solid condition, coupled with that of their crystalline form-so as to elucidate the matter. The following research is a first communication on this subject.

I. Nitro- and Nitroso-Derivatives of the Benzene-Series.

In consequence of some crystallographic facts, I intended long ago to make a special study of morphotropic action of NO_2 and NO substitution in organic molecules. The matter became still more important to me by the observation of the transformation of *o*-Nitrobenzaldehyde into crystallised *o*-Nitrobenzoic acid under the influence of light, and by a recent treatise of BRUNI and CALLEGARI (Gazz. Chim. It. (1904) 34. II, 246) who determined this formation of solid solutions according to cryoscopic determinations. These investigators arrive at the following conclusions :

1. As a rule aromatic nitrosoderivatives may form solid solutions with the corresponding nitroderivatives.

2. In those solid solutions, also in the liquid ones which have a green colour the nitroso-compounds have the simple molecular size.

It was particularly the first conclusion, which I wanted to submit to a further investigation.

a. *Paranitrodiethylaniline and Paranitrosodiethylaniline.*

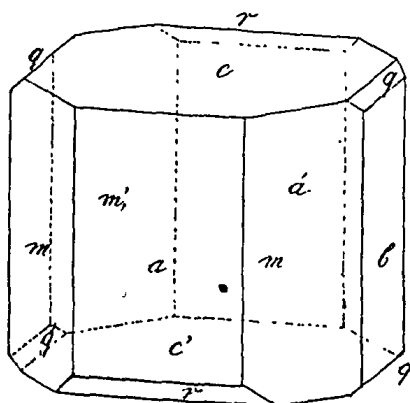
First of all I have extended the investigations *paranitrodiethylaniline* by SCHRAUF and myself¹⁾. As I could only get proper crystals of the nitroso-derivative from ethyl-acetate + ligroïne it was necessary to obtain the crystals of the nitro-derivative from the same solvent in order to get strictly comparable preparations.

1. *p*-Nitrodiethylaniline.

$\text{C}_6\text{H}_4(\text{NO}_2).\text{N}(\text{C}_2\text{H}_5)_2$; meltingpoint: $73^\circ,6$.

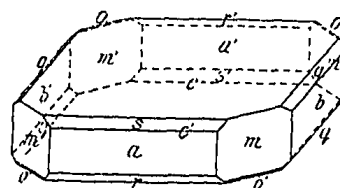
Crystals from ethyl-acetate + ligroïne. (Fig. 1).

Fig. 1.



p-Nitrodiethylaniline, from ethyl-acetate.

Fig. 2.



p-Nitrodiethylaniline, from ethyl-alcohol.

¹⁾ JAEGER, Z. f. Kryst. 40. 127. (1905); cf *ibid.* 11, 105, Ref.

Brownish-yellow crystals, short prismatic or somewhat extended towards the b axis and flattened towards $\{100\}$ with a beautiful reddish-violet reflexion on $\{101\}$.

Monoclinic-prismatic.

$$a : b : c = 1,0342 : 1 : 1,9788.$$

$$\beta = 80^{\circ}34'.$$

The measurements are identical with those formerly given by me. The habitus of the crystals is, however, different from those previously obtained from alcohol (Fig. 2): c and m give ideal reflexes; a very good, but often somewhat curved; c alone has a violet reflexion; the reflex is coloured light-lilac. Etch-figures on $\{100\}$ corresponded with the indicated symmetry.

Very completely cleavable parallel $\{001\}$; fairly so towards $\{010\}$ with conchoidal fracture plane.

Optical behaviour. The optical behaviour of the compound is very interesting. (Fig. 3).

First of all the crystals are strongly pleochroic; on $\{001\}$, sulphur-yellow and blood red; the inflexion indicates the direction of the vibration of the polarised rays; on $\{010\}$ yellow and orange; on $\{100\}$ yellow and orange-yellow. On $\{001\}$ are seen in convergent light two red absorption hyperboles like the opening arms of an axial cross.

On $\{100\}$ an eccentric axial image is visible, the axial angle is very small so that there is apparently present the image of a monaxial crystal with a crossing of the axial planes for red and green light. The axes for the red lie in a plane $\parallel b$ -axis, for the green in one $\parallel c$ -axis. The angle for the red rays is smaller than that of the green rays. The double refraction is positive; the first diagonal inclines to the normal m in the plane of symmetry; on $\{100\}$ there are, therefore, at the same time an inclined and a horizontal dispersion.

The angle of inclination is somewhat larger than in the case of the nitroso-derivative.

2. p-Nitrosodiethylaniline.

Some time ago ¹⁾ I made some preliminary communications on paranitrosodiethylaniline $C_6H_4(NO)N(C_2H_5)_2$, melting point $82^{\circ},2$. I have since succeeded in obtaining this compound in a form more

¹⁾ F. M. JAEGER. Ueber morphotropische Beziehungen bei den in der Amino-Gruppe substituirten Nitro-Anilinen. Z. f. Kryst. 40 (1904) 112—146.

suitable for investigation, so as to be able to make a clear comparison with the corresponding *para*-nitro-derivative.

The said crystals had the appearance of small emerald green rectangular plates, which were most readily obtained from acetone. They are very poor in combination forms and only exhibit $a = \{100\}$ predominating, $m = \{110\}$ and $b = \{010\}$ whilst $a = \{100\}$ is generally present in a rudimentary condition. They were determined as monoclinic-prismatic with $\beta =$ about $85^{\circ}53'$ and $a.b = 10166 : 1$; on $\{100\}$ an interfering image is visible with slight inclination to the normal on that plane, the axial angle is small, the dispersion an average of $q < v$ round the sharp bissectrix, the double refraction is positive.

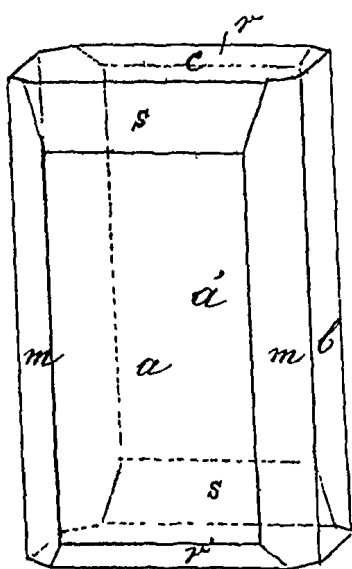
More accurate investigations have, as will be shown, practically confirmed these data. I obtained the improved material from a mixture of ethyl-acetate and ligroine, in which the compound was dissolved on warming. On slow evaporation small rectangularly bounded, thicker plates or also emerald green prisms are formed, which on some planes possess a splendid violet reflexion. They exhibit a particular lustre and but, rarely a curvature of $\{100\}$, therefore very accurate determinations could be executed.

The symmetry is *monoclinic-prismatic*: the axial relation:

$$a : b : c = 1,0178 : 1 : 1,9611.$$

$$\beta = 85^{\circ}43'.$$

Fig. 4.



p-Nitroso-diethylaniline.

Forms observed. $a = \{100\}$, broadest developed of all and well reflecting, sometimes a little curved; $m = \{110\}$ and $b = \{010\}$, about equally developed, but b generally a little broader, although sometimes much narrower than m and much sharper reflecting with light-violet reflex; $c = \{001\}$, with ideal reflexion also with a violet reflex image; $r = \{\bar{1}02\}$, lustrous, mostly narrower, sometimes a trifle better developed and sharply reflecting; the reflexes are often violet, mostly, however, colourless or yellowish; $s = \{101\}$, broad but very dull and only approximately measurable; $t = \{\bar{1}.0.13\}$, very narrow in vicinal form has been observed in a few cases.

The habitus of the crystals is elongated along the vertical axis with flattening towards $\{100\}$.

| | <i>Measured :</i> | <i>Calculated .</i> |
|---------------------------------------|----------------------|-----------------------------|
| $a : c = (100) : (001) =$ | $85^{\circ} 43'$ | — |
| $a : m = (100) : (110) =$ | $45 \ 25\frac{1}{2}$ | — |
| $c : r = (001) : (\bar{1}02) =$ | $45 \ 59\frac{1}{2}$ | — |
| $r : a = (\bar{1}02) . (\bar{1}00) =$ | 48 19 | $48^{\circ} 17\frac{1}{2}'$ |
| $a : s = (100) . (101) =$ | 26 39 | 26 29 |
| $s : c = (101) . (001) =$ | 59 4 | 59 14 |
| $c : m = (001) . (110) =$ | 87 5 | 87 0 |
| $m : b = (110) . (010) =$ | 44 33 | $44 \ 34\frac{1}{2}$ |
| $m : r = (\bar{1}10) : (\bar{1}02) =$ | 62 11 | $62 \ 9\frac{2}{3}$ |
| $m : s = (110) : (101) =$ | 52 0 (circa) | 51 5 |

The crystals cleave very completely towards {001} with a lustrous separation plane; incompletely towards {010} with a conchoidal fracture. Etch figures were not obtained.

Optical behaviour. The compound exhibits interesting optical properties.

First of all the splendid, violet reflexion of the planes {001}, {010} and $\{\bar{1}02\}$, which is wanting on the other planes. This reflexion is not due to a streaking of these planes. If we cleave a crystal along c or b the plane of separation also has that reflexion and a streak made with the crystals on porcelain also exhibits the same phenomenon. The light reflexes of the goniometer lamp on these planes are coloured a beautiful pale lilac; on the other planes white, sometimes yellowish.

Further, the compound exhibits on {100}, {010} and {010} the pleochroic behaviour as seen in Fig. 5; the inflexion again indicates the direction of the vibration of the two polarised rays, which arrive along the normal on the respective plane. On {100} a difference is only observable with thicker crystals, on {001} the colours are light-green and dark, somewhat bluish-green, on {010} the difference is most pronounced, namely light-green and dark violet, the latter colour is indeed, as I noticed, no surface reflexion but the colour of the phase in transmitted light. On {001} feeble absorption bundles of hyperbolic form are observable resembling an axial cross opening when the table is turned.

The optical axial plane is nearly horizontal, the acute bissectrix makes a small angle with the normal on {100}. In convergent light a very fine axial image is visible with a small axial angle and an average dispersion of rhombic character; the dispersion of the said diagonal is $q < v$, the double refraction is positive.

Calling the crystallonomic axes respectively a, b, c the optical

orientation of the elasticity-ellipsoid is therefore in the same order: γ, β, α in which $\alpha > \beta > \gamma$. The double refraction is feeble.

On {100} and {001} orientated extinction; on {010} the very small inclined angle of the elasticity axis with the vertical axis could not be sharply defined on account of the strong absorption; it is not distinguishable from 90° .

The specific gravity of the crystals was found to be 1.240 at 15° ; the equivalent volume is, therefore, 143.53 and the topical axes become:

$$\chi : \psi : \omega = 4,2363 : 4,1623 : 8,1626.$$

The complete *isomorphy* of *p-Nitrodiethylaniline* and *p-Nitrosodiethylaniline* is therefore firmly established. The properties of both substances are given here by way of a comparison.

p-Nitrodiethylaniline :

Monoclinic-prismatic.

$$a : b : c = 1,0342 : 1 : 1,9788.$$

$$\chi : \psi : \omega = 4,4276 : 4,2807 : 8,4710.$$

$$d = 1,225$$

$$v = 158,36$$

Angular values :

$$(110) : (100) = 45^\circ 34'$$

$$(100) : (10\bar{2}) = 51^\circ 13'$$

$$(100) : (001) = 80^\circ 34'$$

In ethyl-acetate + ligroine the habitus is flattened towards {100} elongated towards the *c*-axis; sometimes towards the *b*-axis.

Very completely cleavable towards {001}, fairly so towards {010}, with a conchoidal fracture.

On {001} violet reflexion.

Optical orientation : γ, β, α .

Double refraction, positive.

On {100} a but little-inclined axial image with small axial angle; axial plane parallel the *b*-axis for the red, parallel the *c*-axis for the green rays; dispersion : $\rho < v$.

Colour : brownish-yellow.

Strongly pleochroic: blood red-orange-yellow.

On *c* absorptionbundles.

p-Nitrosodiethylaniline :

Monoclinic-prismatic.

$$a : b : c = 1,0178 : 1 : 1,9611.$$

$$\chi : \psi : \omega = 4,2363 : 4,1623 : 8,1626.$$

$$d = 1,240$$

$$v = 143,53$$

Angular values :

$$(110) : (100) = 45^\circ 25\frac{1}{2}'$$

$$(100) : (10\bar{2}) = 48^\circ 17\frac{1}{2}'$$

$$(100) : (001) = 85^\circ 43'$$

In ethyl-acetate + ligroine the habitus is flattened towards {100} and elongated towards the *c*-axis.

Very completely cleavable towards {001}, fairly so towards {010} with conchoidal fracture.

On {001}, and on {010}, $\{10\bar{2}\}$ violet reflexion.

Optical orientation : γ, β, α ,

Double refraction, positive.

On {100} a but little-inclined axial image with small axial image; axial plane parallel the *b*-axis; rhombic dispersion : $\rho < v$.

Colour : emerald green.

Strongly pleochroic: violet-pale green-bluishgreen.

On *c* absorptionbundles.

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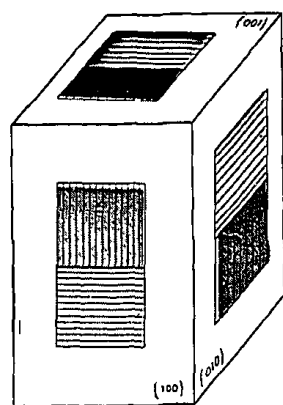


Fig 3.

Pleochroism of p-Nitro-diaethyl-aniline

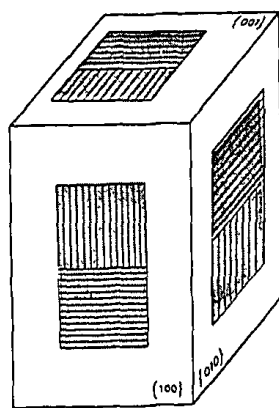


Fig 5

Pleochroism of p-Nitroso-diaethyl-aniline

There is not the least doubt that the two substances possess a quite analogous structure; cleavability, optical orientation whilst the nature of the surface of the crystalplanes is quite in agreement.

From mixed solutions of the two components are formed small greenish-black mixed crystals with a vivid steel-blue reflexion.

As generally happens in the case of most isomorphous mixtures, the crystallisation power is considerably smaller than with each of the components separately. Under the microscope such mixed crystals consist of thin olive-green little plates, which on their predominating plane show little or no pleochroism. In convergent light a splendid interfering image may be observed: slight inclination to the normal on the horizontal plane, elliptical rings, and small axial angle, larger however than in the two components. The double refraction is positive: the dispersion has a rhombic character and shows: $\rho < r$.

From the last motherliquors are deposited mixed crystals of a lighter shade representing silky needles as those above with less surface reflexion. Otherwise they are optical continuations of the above described mixed crystals. From mixtures of the two components in a melted condition these mixed crystals depose on the sides of the testtube in a fine steel-blue lustrous condition.

The behaviour of the two isomorphous substances in the liquid condition is elucidated by the investigation of the melting curve of binary mixtures. On account of the dark colour of the fusion, the course of the solidification curve was traced by the graphical method; the determinations were made as usual in the VAN EYK apparatus. It should be noticed that all these fusions solidify to solid phases, which also exhibit a splendid violet or blue reflexion.

The nitroderivative has a greater latent heat of fusion than the nitrosoderivative; in both cases the caloric effect was, however, very readily observable in the solidification. The lower solidifying line can by no means be determined so sharply as the upper one.

It was found that:

A mixture of 100 % of *p-Nitro* and 0 % *p-Nitroso*-derivative melted at 73°,6.

A mixture of 85,14 % *p-Nitro*- and 14,86 % *p-Nitroso*-derivative commences to solidify at 75°,2 and completely solidifies at 74°,9.

A mixture of 72,5 % of *p-Nitro*- and 27,5 % *p-Nitroso*-derivative commences to solidify at 76°,2 and completely solidifies at 75°,9.

A mixture of 54,4 % of *p-Nitro*- and 45,6 % of *p-Nitroso*-derivative commences to solidify at 77°,6 and completely solidifies at 77°,3.

A mixture of 38,64 % of *p-Nitro*- and 61,36 % *p-Nitroso*-derivative commences to solidify at 78°,2 and completely solidifies at 77°,9.

A mixture of 10,0 % *p-Nitro*- and 90,0 % of *p-Nitroso*-derivative commences to solidify at 80°,8 and completely solidifies at 80°,6.

A mixture of 0 % of *p-Nitro*- and 100 % of *p-Nitroso*-derivative melted at 82°,2.

The composition is given in molecule-percents.

In fig. 6 the course of the melting curve is represented graphically and the double line for the initial and final solidifying points is shown. It will be seen that the character of the line points to a continuous series of mixed crystals; the average temperature-interval between initial and final solidification amounts to about 0°,3.

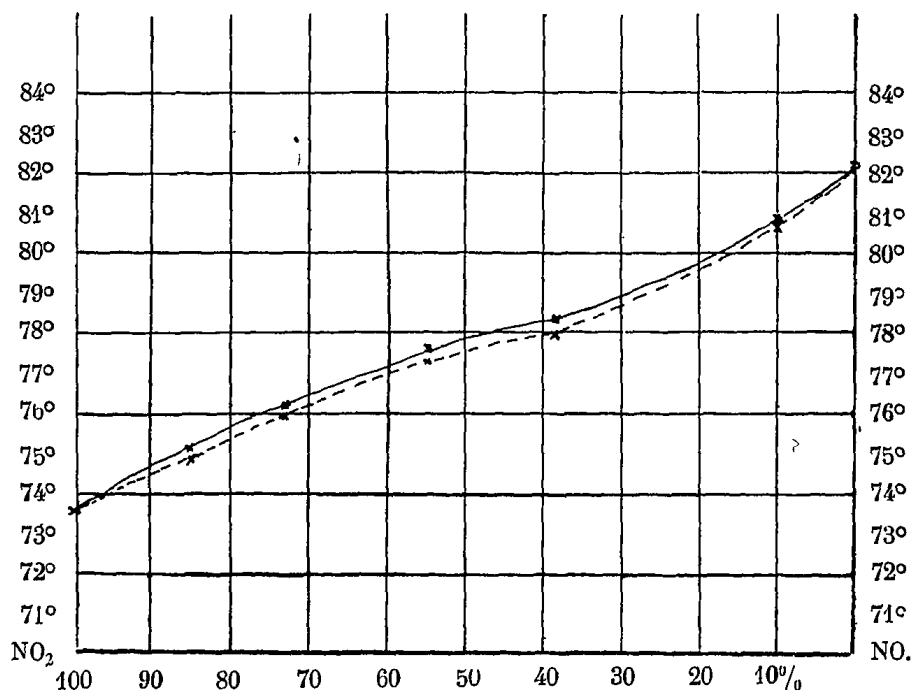


Fig. 6.

The result of the research reveals the complete isomorphy of *p-Nitro-diethylaniline* and *p-Nitroso-diethylaniline* and also their complete miscibility in the solid state.

Chemistry. — “*On Orthonitrobenzyltoluidine*”. By Dr. F. M. JAEGER.
(Communicated by Prof. A. F. HOLLEMAN).

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

Some time ago the *o-Nitrobenzyl* derivate of *para-toluidine*, (melting point 72° C.) was investigated by NORDENSKJOLD, who described it as being *tetragonal* with the parameter-relation $a:c = 1:0,6230$; the compound exhibits only one combination-form, namely {111} and is optically monaxial: positive. (Bull. Geol. Instit. Upsala, (1892), 84, also Ref. Zeits. f Kryst. **24**, 147).