Chemistry. — *"On some Condensation-products of Aromatic Alde-hydes and Amines."* By Prof. F. M. Jaeger.

(Communicated at the meeting of May 29, 1920).

§ 1. Although, according to Hantzsch's and Werner's theoretical views, the existence of stereoisomeric forms should be possible in the case of condensation-products of aromatic aldehydes and amines of the type: $R_1—CH = N—R_2$, yet it had appeared impossible during a long time to find with certainty[1]) cases of such isomerism with these so-called "bases of Schiff". In 1906, however, Anselmino[2]) described some cases, where substances of this kind were met with in two different crystalline modifications, which at the same time appeared to be strongly different in colour, being red and yellow. The author concluded from his investigations that no true *dimorphism* in the common sense of the word was present here, but that rather a chemical *isomerism* had to be supposed. The arguments brought to the fore by him for demonstrating that neither enantiotropic, nor monotropic relations whatsoever between the crystalforms of the red and yellow modifications of *o-oxy-m-methyl benzylidene-aniline* should be present, can, however, in our opinion hardly be estimated to be convincing. It seems notwithstanding this to be true, that the deviating chemical character of the yellow and the red forms, of which the last reacts much more easily with reagents attacking the *HO*-groups of the molecule, points in this case really to a chemical isomerism, in which to the red modification must then be attributed probably the *trans*-configuration, in the sense of Werner's theory.

In the light of the interpretations given of the more recent investigations of crystals by means of Röntgenrays, the question about the discrimination between cases of "physical", in contrast with "chemical" isomerism, seems to have no longer any real significance, at least for solid matter: undoubtedly each modification of polymorphous substances will in the solid state also possess a definite spatial configuration differing from that of the other modification; and probably this difference will, at least partially, be preserved in the state of

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[1]) A. Hantzsch and O. Schwab, Ber. d. d. Chem. Gec., **34**, 822, (1901).
[2]) O. Anselmino, Ber. d. d Chem. Ges. **38**, 3989, (1906); **40**, 3465, (1907).

solution, and almost certainly in the molten mass. But only, if such differences be really stated in the liquid phases to a measurable
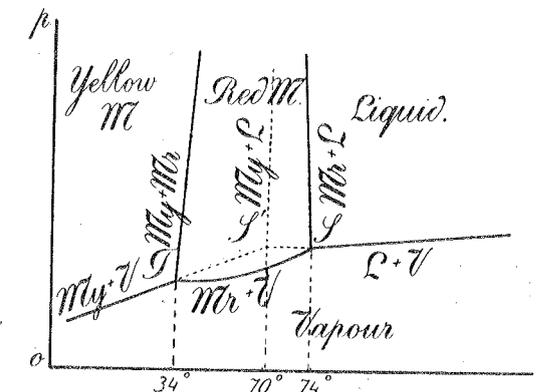

Fig. 1.

degree, it appears rational to speak of two kinds of chemical molecules.

However, disregarding for a moment their chemical isomerism, from a *crystallographical* point of view, the red and yellow modifications of the base mentioned, seem, in our opinion, to be related as true enantiotropic forms, as e.g. is the case with monoclinic and rhombic *sulphur*. The *irr*eversibility observed by Anselmino is evidently only an *apparent* one, caused by intensive retardation phenomena: the transition-temperature: yellow ⇄ red, is 34° C., while the meltingpoint of the red modification is found to be 74° C. and that of the (metastable) yellow form 70° C. By this interpretation all relations existing between the red and yellow forms, as observed by Anselmino, may be explained in an unambiguous way.

§ 2. With respect to the crystallographical properties of these compounds, in the first place the numbers relating to the derivatives already obtained by Anselmino, may be recorded in the following. They were already obtained by us in 1906, but by special circumstances their publication has been postponed till now.

The condensation-product of *p-homosalicylaldehyde* (from *p-cresol*) and *aniline*: **o-oxy-m-methyl-benzylidene-aniline**:

$$CH_3 \quad \diagdown \quad CH=N—C_6H_5, \quad OH$$
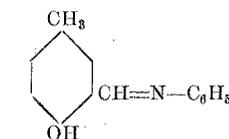
occurs in two forms, of which the one is *yellow*, the other *red*, and which were studied already formerly by H. Traube and F. Schmeling[1])

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[1]) F. Schmeling, Diss. Greiswald, (1905), p. 56, 58.

in detail. The *yellow* (metastable) modification, melting at 70° C., is rhombic-bipyramidal, with the parameters: $a : b : c = 0,3732 : 1 : 0,4228$, and the forms: {010}; {011}; {101}; {102}. Its birefringency is of positive character; the optical axial plane is parallel to {100}. The crystals show a cleavability parallel to {100} and {010}; their specific gravity at 17° C. is: $d_{4^\circ} = 1,243$, from which the equivalent-volume is calculated at: 169,75, and the topical parameters at: $\chi : \psi : \omega = 3,8269 : 10,2471 : 4,3322$.

The *red* modification, which melts at 74° C., and to which the yellow form changes at 34° C., is monoclinic-prismatic. The parameters published by the author do *not* agree with those calculated from his angular values: they are really:

$$a : b : c = 0,2362 : 1 : 0,6579;$$
$$\beta = 74°9\tfrac{1}{2}',$$

if the same angles be used as by the author mentioned. The occurring forms have the symbols: {010}, {001}, {110}, and {011}. The optical axial plane of these strongly pleochroïtic, negatively birefringent crystals is perpendicular to {010}; the cleavage occurs parallel to {001} and {010}. The specific weight of the crystals is: 1,263 at 17° C.; the equivalent-volume is therefore: 167,06, and the topical parameters are calculated at: $\chi : \psi : \omega = 2,4511 : 10,3770 : 6,8271$. The transition of the yellow into the red crystals occurs in such a way, that the two modifications are rigorously orientated with respect to each other in two different ways, the faces of {010} of the two forms remaining always parallel to each other; — a fact clearly demonstrating the intimate relation of their internal structures. It is worth remarking here, that the dimensions in the direction of the b-axes in both modifications appear to be almost the same (namely: 10,3, as topical parameter), while the intergrowth of the α- and β-crystals parallel to {010} occurs in such a way that either the c-axis of the one modification coincides with the c-axis of the other, or the a- and c-axes of the crystals appear to be interchanged, although in these directions the topical parameters do not show a direct relation to each other.

§ 3. II. o-Methoxy-m-methyl-benzylidene-aniline.

This substance, which has the composition:

$$CH_3$$
$$\bigcirc$$
$$CH=N-C_6H_5$$
$$OCH_3$$
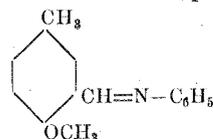
was obtained from the foregoing by means of methylsulphate at 40° C. It melts at 70° C., and crystallizes from ligroin in beautiful, pale yellow, transparent crystals.
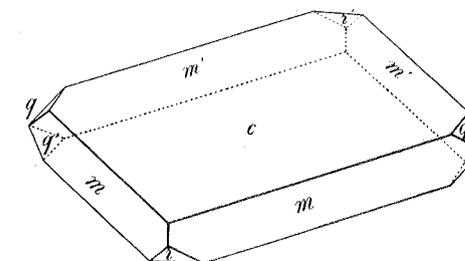

Fig. 2. *o-Methoxy-m-methyl-benzylidene-aniline.*

Monoclinic-prismatic.
$$a : b : c = 1,2792 : 1 : 1,0509;$$
$$\beta = 76° 59\tfrac{1}{3}'.$$

Forms observed: $c = \{001\}$, large and lustrous; $m = \{110\}$, yielding good reflexes, like $q = \{011\}$ also; $r = \{\bar{1}01\}$, small, but well determinable. The aspect of the crystals is tabular parallel {001}.

Angular values:			*Observed:*	*Calculated:*
$c : q = (001) : (011) =$	*		45° 39′	—
$c : m = (001) : (110) =$	*		81 54	—
$m : m = (110) : (1\bar{1}0) =$	*		102 31	—
$c : r = (001) : (\bar{1}01) =$			44 22	44° 27′

No distinct cleavage was found.

The specific weight of the crystals at 16° C. was: 1,166; the molecular volume is therefore: 192,96, and the topical parameters are: $\chi : \psi : \omega = 6,7561 : 5,2813 : 5.5502$. The form-analogy with the red modification of the foregoing substance is undeniable.

§ 4. III. o-Oxy-m-methyl-α-anilido-ethylbenzene.

This compound, which melts at 90° C., was obtained from the first by means of two molecules of methylmagnesium-iodide in boiling etheric solution, and subsequent decomposition of the product with water. It has the formula:

$$CH_3$$
$$\bigcirc$$
$$CH(CH_3)-NH-C_6H_5,$$
$$OH$$
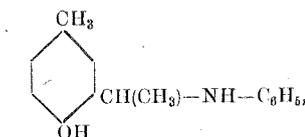
and crystallizes from ligroin in very small, colourless, and almost rectangular plates.

Monoclinic-prismatic.

$$a : b : c = 0,2682 : 1 : 0,7254.$$

$$\beta = 85° 47'.$$

Forms observed: $b = \{010\}$, predominant; $m = \{110\}$ and $a = \{100\}$, well reflecting. In the zone of $q = \{011\}$, $s = \{012\}$ and $c = \{001\}$, the angular measurements ordinarily are not so accurate as in the other zones; commonly $q = \{011\}$ is the best developed. The aspect of the crystals is that of thin plates parallel to $\{010\}$.
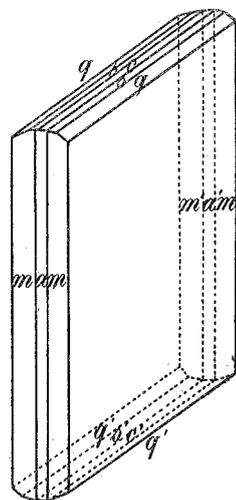

Fig. 3. *o-Oxy-m-methyl-α-anilido-ethylbenzene.*

Angular values:		*Observed*:		*Calculated*:
$b : m = (010) : (110) =$*	75°	1½′		—
$b : q = (010) : (011) =$*	54	7		—
$a : q = (100) : (011) =$*	86	35		—
$a : c = (100) : (001) =$	86	1½	85°	47′
$s : q = (012) : (011) =$	15	56	16	0
$s : s = (012) : (0\bar{1}2) =$	40	3½	39	46½
$m : q = (110) : (011) =$	78	0	77	56
$m : a = (110) : (100) =$	14	58½	14	58½

A cleavage exists parallel to $\{001\}$.

The specific weight of the crystals at 17° C. is: 1,107; the equivalent-volume therefore: 205,06. The topical parameters are: $\chi : \psi : \omega = 2,7319 : 10,1861 : 7,3890.$

On $\{010\}$ the extinction-angle is 43° with respect to the direction of the c-axis in the quadrant behind. Probably the optical axial plane is parallel to $\{010\}$.

§ 5. IV. o-Methoxy-m-methyl-α-anilido-ethylbenzene.

This substance was obtained from the corresponding benzylidene-aniline by means of methylmagnesium-iodide and subsequent decomposition by water.

The compound, which has the formula:

CH₃

CH(CH₃)—NH—C₆H₅

OCH₃

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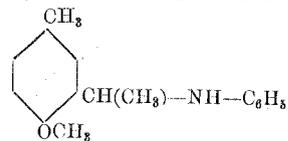
melts at 78° C., and crystallizes from ligroin in big, colourless, strongly refracting crystals of tabular or prismatic aspect. Ordinarily
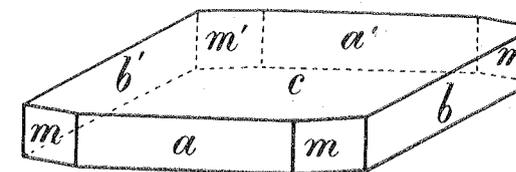

Fig. 4. *o-Methoxy-m-methyl α-anilido-ethylbenzene.*

they manifest curved faces, exact measurements thus being rather difficult.

Rhombic-bipyramidal.

$$a : b = 0,3301 : 1.$$

Forms observed: $c = \{001\}$ predominant; $a = \{100\}$ and $b = \{010\}$, yielding good reflections; $m = \{110\}$, small, but lustrous.

| *Angular values*:		*Observed*:		*Calculated*:
$a : m = (100) : (110) =$*	18°	16		—
$b : m = (010) : (110) =$	71	44	71°	44′

All other angles are 90°.

A good cleavage was found parallel to $\{100\}$ and $\{010\}$.

The optical axial plane is $\{100\}$, with the b-axis as first bisector. The angle of the optical axes is very small, with extraordinarily strong dispersion: $\varrho > v$; the apparent angle of the axes in oil $(n = 1,54)$ was about 48° for the red, and about 25° for the violet rays. On $\{001\}$ corrosion-figures were obtained of rectangular form, in agreement with the adopted crystallographical symmetry.

At 16° C. the specific of the crystals was: 1,098; the equivalent-volume therefore, being: 219,49.

§ 6. V. o-Oxy-benzylidene-aniline. [1])

This compound, having the formula:

CH=N—C₆H₅

OH

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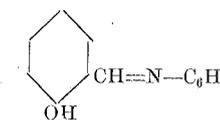
[1]) Conf. also: L. DUPARC, Ann. d. Chemie, **266**, 140 (1891); here b is taken as $\{001\}$, the axial ratio, therefore becoming: $c' : b' : a' = 4,586 : 1 : 2, 1922$. (In DUPARC's paper $a : b$ is erroneously taken ten times too small, and the a- and c-axes are interchanged. The crystals are identical with ours.

and melting at 50°,5 C., was obtained from salicylaldehyde and aniline.

The substance is *dimorphous*: it occurs in a less stable rhombic α-modification, and in a monoclinic β-form, which is obtained in most cases; both modifications are yellow.
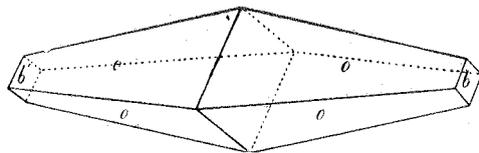
1. α-Modification.

Fig. 5. *o-Oxy-benzylidene-aniline.*
(α-*Modification*).

From ligroin this modification crystallizes in most cases in the form of big, yellow, almost always opaque and flattened bipyramids.

Rhombic-bipyramidal.

$$a : b : c = 0,4729 : 1 : 0,2188.$$

Forms observed: $o = \{111\}$, big, but badly reflecting; $b = \{010\}$, small, yielding good reflexes. The crystals obtained from a solution in methyl-alcohol showed also a prism $m = \{130\}$, the faces of which gave good images.

Angular values:	*Observed:*	*Calculated:*
$o : o = (111) : (1\bar{1}1) =$ *	22°28½′	—
$o : o = (111) : (\bar{1}11) =$ *	48 39	—
$o : o = (111) : (11\bar{1}) =$	125 55	125°47′
$o : b = (111) : (010) =$	78 46	78 46
$m : b = (130) : (010) =$	34 59½	35 11

No distinct cleavage was found.

The specific weight of these crystals was: 1,087 at 16° C.; the equivalent-volume is thus: 181,23, and the topical parameters are calculated at: $\chi : \psi : \omega = 5,7005 : 12,0539 : 2,6375$.

2. β-Modification.

The crystals of the α-modification are easily transformed into those of the β-form by recrystallisation. If, however, the long needles of the β-modification thus obtained, are again recrystallized from methyl-alcohol, they are again changed into the bipyramids of the α-form.

Strongly refracting, yellow needles.

Monoclinic-prismatic.

$$a : b = 2,4641 : 1 ;$$
$$\beta = 26° 2½′$$

Forms observed: $m = \{110\}$, large and lustrous; $a = \{100\}$, narrower; $c = \{001\}$, well developed. Moreover, again a negative pyramid and a doma are observed, which, however, cannot be determined more precisely. It is for this reason, that the occurring face c was taken as $\{001\}$, although this form represents certainly not a basal face, but a horizontal prism.

Angular values:	*Observed:*	*Calculated:*
$m : a = (110) : (100) =$ *	47° 15′	—
$a : c = (100) : (001) =$ *	26 2½	—
$m : c = (110) : (001) =$	52 40	52° 25′

No distinct cleavability was observed.

The specific weight of the crystals was: 1,184 at 17° C.; the molecular volume is, therefore, 166,38.
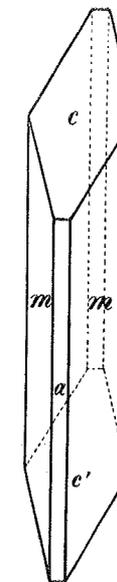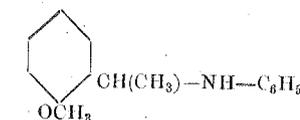

Fig. 6. *o-Oxy-benzylidene-aniline.* (β-*Modification*).

§ 7. VI. α-Anilido-ethyl-anisol.

This compound was prepared from the just mentioned by means of methylmagnesium-iodide, etc. It has the formula:

and melts at 46° C.

From ligroin badly developed, strongly refracting needles are deposited, which allow only approximate measurements.

Rhombic-bipyramidal.

$$a : b : c = 0,884 : 1 : 0,465.$$

Forms observed: $t = \{110\}$, $m = \{320\}$, $p = \{210\}$, and $n = \{520\}$, all about equally narrow, and yielding multiple reflexes; $q = \{011\}$, smaller, and badly reflecting. The aspect of the crystals is elongated in the direction of the c-axis.

Fig. 7 *Anilido-ethyl-anisol.*

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Angular values: *Observed:*   *Calculated:*

$$
\begin{array}{llrr}
t:t = (110):(\bar{1}10) =^* & 97°\ 4' & — \\
q:q = (011):(0\bar{1}1) =^* & 49\ 51 & — \\
t:m = (110):(320) = & 11\ 12 & 11°\ 0' \\
m:p = (320):(210) = & 6\ 22 & 6\ 37 \\
p:n = (210):(520) = & 8\ 40 & 8\ 31 \\
\end{array}
$$

A distinct cleavability was not stated.

The specific weight of the crystals was: 1,141 at 18° C.; the equivalent-volume is thus: 176,16, and the topical axial ratios are calculated at $\chi : \psi : \omega = 6,6649 : 7,5395 : 3,5059$.

§ 8. VII. p-Methoxy-benzal-aniline (*Anisal-aniline*).

This substance, which melts at 63° C., and possesses the constitution:

OCH₃

CH=N—C₆H₅
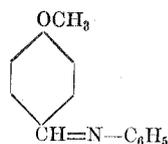
was obtained from anisaldehyde and aniline.

It crystallizes from ligroin in colourless, well developed, very transparent crystals, having the odour of anisol.

Monoclinic-prismatic.

$$a : b : c = 1,5745 : 1 : 0,8063;$$
$$\beta = 65°21'$$

Forms observed: $c = \{001\}$, well developed and yielding splendid reflexes; $q = \{011\}$, $r = \{\bar{2}01\}$, and $o = \{\bar{2}11\}$, giving all sharp mirror-images; $m = \{110\}$ and $a = \{100\}$, somewhat narrower, but well measurable. The form a is often absent, or only developed with a single face, while o and r are often very narrow. The aspect of the crystals is that of thick prisms with an elongation parallel to the c-axis. They are generally well built.
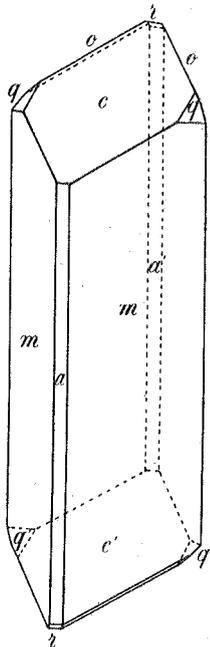

Fig. 8. *Methoxy-benzal-aniline.*

Angular values: *Observed:*   *Calculated:*

$$
\begin{array}{llrr}
c:a = (001):(100) =^* & 65°\ 21' & — \\
c:q = (001):(011) =^* & 36\ 14 & — \\
m:m = (110):(1\bar{1}0) =^* & 110\ 6\tfrac{1}{2} & — \\
c:r = (001):(\bar{2}01) = & 58\ 30\tfrac{1}{2} & 58°\ 23\tfrac{1}{2} \\
o:r = (\bar{2}11):(\bar{2}01) = & 33\ 57\tfrac{1}{2} & 33\ 51 \\
m:q = (110):(011) = & 47\ 18 & 47\ 22\tfrac{1}{2} \\
o:m = (\bar{2}11):(\bar{1}10) = & 44\ 7 & 43\ 54 \\
c:m = (001):(110) = & 76\ 7\tfrac{1}{2} & 76\ 10\tfrac{1}{2} \\
m:q = (\bar{1}10):(0\bar{1}1) = & 73\ 3 & 73\ 2\tfrac{1}{4} \\
\end{array}
$$

Perfect cleavable parallel to {001}.

An apparently second modification was, on more detailed investigation, really identical with the one described. However, yet another, truly polymorphic modification was observed [1]), crystallizing in extremely thin, unmeasurable, small plates with normal extinction; they are first deposited from solutions, but are rapidly changed into the crystals described in the above.

The needles here investigated, have oblique extinction: on m at an angle of $22\tfrac{1}{2}°$ with the direction of the c-axis.

The specific weight of the crystals at 17° C. was: 1,165; the equivalent-volume is thus: 181,11.

Topical parameters: $\chi : \psi : \omega = 8,4931 : 5,3942 : 4.3494$.

We are occupied with tentatives to obtain condensation-products of other aldehydes and amines of the aromatic series, with the purpose to find other cases of polymorphism or isomerism with bases of this kind. Perhaps we shall be able to return to this question within a not too remote future.

Laboratory for Inorganic and Physical
Groningen, May 1920.   *Chemistry of the University.*

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[1]) H. OTT, Monatshefte f. Chemie, **26**, 340 (1905).