

pressure in the series of the liquid-vapour equilibria is but little probable. At the moment there only seems an indication that the case occurs with  $\text{PH}_4\text{Cl}$ .

If the line  $HM$  is situated much more towards the side of  $A$  it might then also happen that the point  $H$  did not occur on the three-phase line of the compound, but on that of the compound  $A$ , so that branch 3 on this line follows on branch 1 and disappears from the three-phase lines of the compound.

In a future communication I will discuss the boiling phenomena of the saturated solutions corresponding with the said branches of the three-phase lines.

**Crystallography.** — "On *Diphenylhydrazine*, *Hydrazobenzene* and *Benzylaniline*, and on the miscibility of the last two with *Azobenzene*, *Stilbene* and *Dibenzyl* in the solid state." By Dr. F. M. JAEGER. (Communicated by Prof. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of October 28, 1905).

The following research was undertaken to furnish a new contribution to the knowledge of the relation of the crystal-symmetry of organic compounds and their power of yielding crystallised mixed phases with each other<sup>1)</sup>. Originally, it only aimed at the investigation of *Hydrazobenzene* and *Benzylaniline* in their connection with the series, investigated by BRUNI, GARELLI, CALZOLARI and GORNI, of *Azobenzene*, *Stilbene*, *Tolane*, *Dibenzyl* and *Benzylideneaniline*, but afterwards, *Diphenylhydrazine*, which is isomeric with *Hydrazobenzene* was also included.

### Diphenylhydrazine.

$(\text{C}_6\text{H}_5)_2\text{N}-\text{NH}_2$ ; melting point:  $44^\circ\text{C}$ .

This compound, which I obtained through the kindness of Prof. S. HOOGWERFF of Delft, crystallises from ligroine in the form of colourless, large, lustrous crystals, which exhibit a rather varying aspect. On exposure to light they rapidly assume a brown colour.

<sup>1)</sup> Compare F. M. JAEGER, These Proc. VII. p. 658.

*Triclinic-pinacoidal.*

$$a : b : c = 0,7698 : 1 : 0,5986.$$

$$\begin{aligned} A &= 89^\circ 13\frac{1}{2}' & \alpha &= 89^\circ 24' \\ B &= 137^\circ 28' & \beta &= 137^\circ 28\frac{1}{2}' \\ C &= 89^\circ 29' & \gamma &= 90^\circ 4\frac{1}{2}' \end{aligned}$$

The approach to *monoclinic* symmetry is very plain.

Forms observed:  $b = \{010\}$ , broad and lustrous;  $m = \{110\}$ , somewhat narrower and reflecting less sharply;  $p = \{1\bar{1}0\}$ , very lustrous and broad;  $c = \{001\}$ , well developed and yielding fairly sharp reflexes;  $o = \{\bar{1}\bar{1}1\}$ , very lustrous and well developed. The crystals are mostly flattened towards  $p$ , or they may be developed isometrically with a slight elongation along the  $c$ -axis. It is peculiar that in the vertical zone the co-related parallel planes of the forms  $m$ ,  $p$  and  $b$  are generally very unevenly developed. Perhaps we may have here a new example of the presence of an acentric crystal; the nature of the surface of the parallel planes is also often different on a plane and its corresponding contreplane.

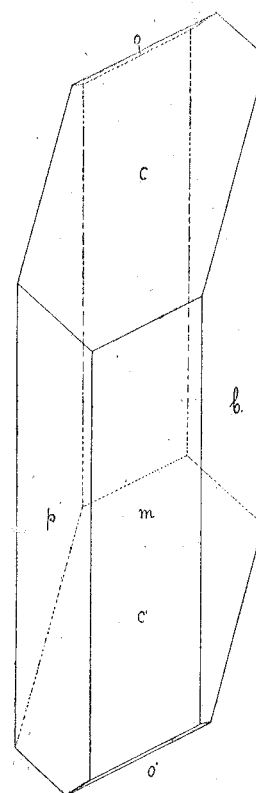


Fig. 1.

(Diphenylhydrazine). Etched figures could not be obtained.

No distinct plane of cleavage.

	Measured:	Calculated:
$b' : p = (0\bar{1}0) : (1\bar{1}0) =$	$* 62^\circ 6'$	—
$b : m = (010) : (110) =$	$* 62^\circ 54\frac{1}{2}'$	—
$b' : c = (0\bar{1}0) : (001) =$	$* 89^\circ 13\frac{1}{2}'$	—
$p : c = (1\bar{1}0) : (001) =$	$* 48^\circ 53'$	—
$o : m' = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	$* 73^\circ 38'$	—
$m : c = (110) : (001) =$	$49^\circ 24'$	$49^\circ 28'$
$o : c = (\bar{1}\bar{1}1) : (001) =$	$56^\circ 54'$	$56^\circ 54'$
$p : o = (1\bar{1}0) : (\bar{1}\bar{1}1) =$	$78^\circ 42'$	$78^\circ 36'$
$o : b' = (\bar{1}\bar{1}1) : (0\bar{1}0) =$	$58^\circ 45\frac{1}{2}'$	$58^\circ 43'$
$p : m = (1\bar{1}0) : (110) =$	$54^\circ 59\frac{1}{2}'$	$54^\circ 59\frac{1}{2}'$

In the vertical zone the situation of the optical elasticity axes was almost parallel to the direction of the  $c$ -axis; but on  $b$  the angle of inclination amounted to about  $10^\circ$ , on  $m$  only about  $1^\circ$ . An axial image could not be observed.

The sp. gr. of the crystals is 1,190 at 16°; the equivalent volume 154,62. Topical axes  $\chi : \psi : \omega = 6,0956 : 7,9182 : 4,7399$ .

### Hydrazo-Benzene.

$C_6H_5 \cdot NH-NH \cdot C_6H_5$ ; melting point: 125° C.

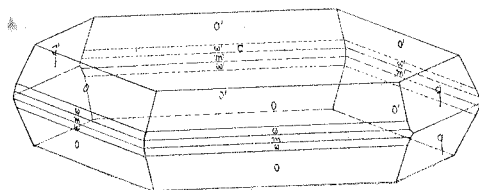


Fig. 2.  
(Hydrazobenzene).

When recrystallised from a mixture of alcohol and ether, the compound forms small, thin, colourless, square plates.

### Rhombic-bipyramidal.

$$a : b : c = 0,9787 : 1 : 1,2497.$$

Forms observed:  $c = \{001\}$ , strongly predominant and very lustrous;  $o = \{111\}$ , sharply reflecting;  $q = \{021\}$ , lustrous, always very small developed;  $\omega = \{221\}$ , narrow;  $m = \{110\}$  very narrow and often wanting altogether. Thin-tabled towards  $c$ .

Measured:	Calculated:
$c : o = (001) : (111) = * 60^{\circ}46'$	—
$o : o = (111) : (\bar{1}\bar{1}) = * 75 14$	—
$c : q = (001) : (021) = 68 11$	$68^{\circ}12'$
$o : \omega = (111) : (221) = 13 45$	$13 36$
$\omega : m = (221) : (110) = 15 27$	$15 38$
$c : m = (001) : (110) = 89 56$	$90 0$
$\omega : \omega = (221) : (2\bar{2}\bar{1}) = —$	$84 41$
$m : m = (110) : (\bar{1}\bar{1}0) = 88 36$	$88 46$
$\omega : \omega = (221) : (2\bar{2}\bar{1}) = 30 58$	$31 16$

Very completely cleavable along  $\{001\}$ .

On  $c$  the situation of the directions of extinction is orientated towards the side  $c : q$ . An axial image could not be observed.

Sp. gr. = 1,158 at 16° C.; the equivalent volume is 158,89.

$$\text{Topical axes : } \chi : \psi : \omega = 4,9567 : 5,0645 : 6,3291.$$

### Benzylaniline.

$C_6H_5 \cdot CH_2-NH \cdot C_6H_5$ ; melting point:  $36\frac{1}{2}^{\circ}$  C.

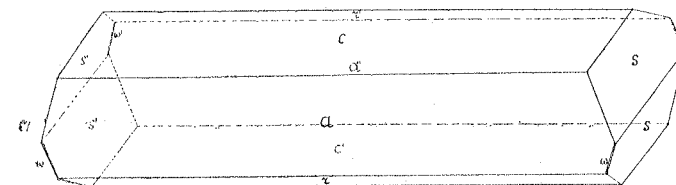


Fig. 3.  
(Benzyl-Aniline).

From ether or alcohol the compound crystallises in large colourless crystals flattened towards  $a$  which, however, never exhibit measurable end planes. The best crystals are obtained from methyl alcohol. They are then mostly twins towards  $\{100\}$  or sometimes parallel-crystallisations. The end planes are generally curved and unsuitable for measurement. With some of the better developed crystals more accurate measurements could be executed.

### Monoclinic-prismatic.

$$a : b : c = 2,1076 : 1 : 1,6422.$$

$$\beta = 76^{\circ}36\frac{1}{2}'.$$

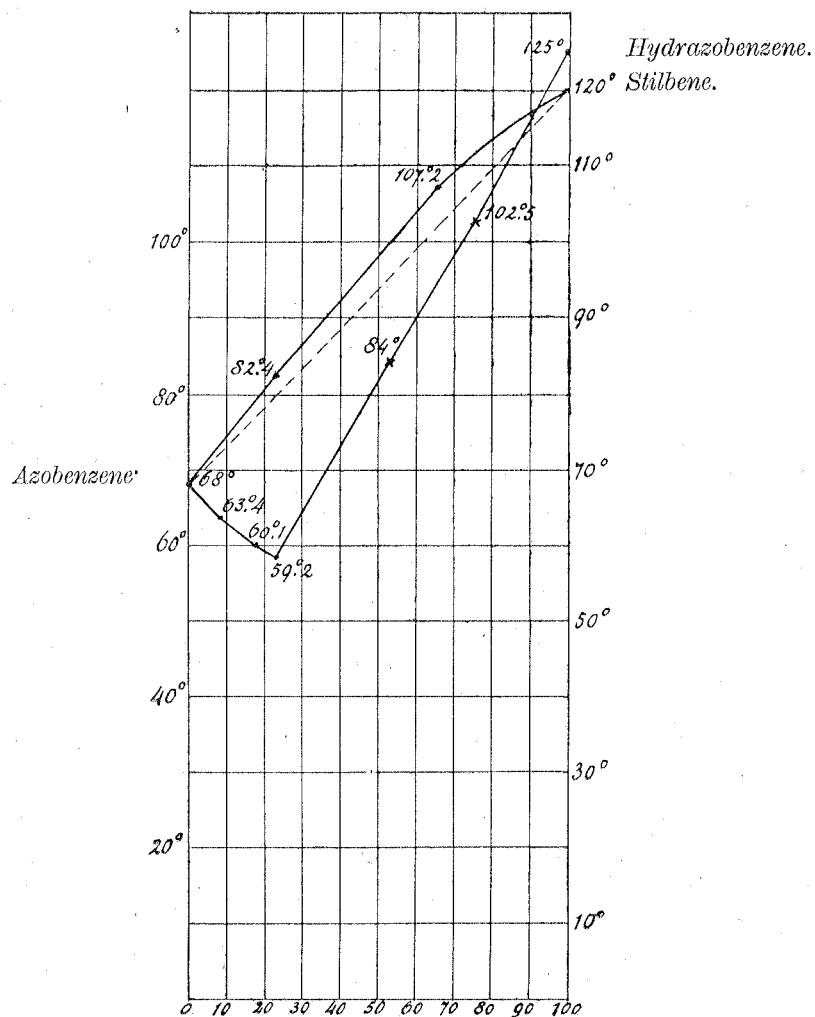
Forms observed:  $a = \{100\}$ , most broadly developed of all and strongly lustrous;  $c = \{001\}$ , somewhat narrower and strongly lustrous;  $s = \{021\}$ , bent and curved, sometimes less opaque and flat;  $r = \{203\}$ , well developed and lustrous;  $\omega = \{24 2 1\}$ , indicated as extremely narrow vicinal form, mostly wanting.

Measured:	Calculated:
$a : c = (100) : (001) = * 76^{\circ}36\frac{1}{2}'$	—
$a : r = (100) : (20\bar{3}) = * 73 31\frac{1}{2}$	—
$c : s = (001) : (021) = * 72 37\frac{1}{4}$	—
$s : s = (021) : (02\bar{1}) = 34 45\frac{1}{2}$	$34^{\circ}45\frac{1}{3}'$
$a : s = (100) : (021) = 93 58$	$93 58$
$r : s = (20\bar{3}) : (02\bar{1}) = 75 1$	$74 59\frac{1}{2}$
$c : r = (001) : (203) = 29 53$	$29 52$

Very completely cleavable towards  $\{001\}$  and  $\{100\}$ . Twins towards  $\{100\}$ .

In the zone of the  $b$ -axis orientated extinction everywhere; the optical axial plane is  $\{010\}$ . On  $a$  and  $c$  a black hyperbola is visible in convergent light; one axis forms with the normal on  $a$  an angle

Fig. 4



Binary meltingpoint lines of Azobenzene + Stilbene  
and of Azobenzene + Hydrazobenzene.

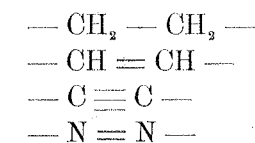
of about  $12^\circ$ . The apparent axial angle in  $\alpha$ -monobromonaphtalene amounts to about  $90^\circ$ . Strong, inclined dispersion with  $q > v$ .

The Sp. Gr. = 1,149 at  $14^\circ$  C.; equivalent vol. = 159,25.

Topical axis:  $\chi : \psi : \omega = 7,6220 : 3,6164 : 5,9389$ .

As regards *Hydrazobenzene* and *Benzylaniline* the following observations must be made.

Some time ago, BRUNI and CIAMICIAN<sup>1)</sup>, and GARELLI and CALZOLARI<sup>2)</sup> concluded, on account of cryoscopic abnormalities, to a formation of mixed phases in the solid state between, *Dibenzyl*, *Stilbene*, *Tolane* and *Azobenzene*, and to the *isomorphogenous* substitution in aromatic molecules of the atomic-combinations:



According to BRUNI and GORNI<sup>3)</sup>, *Benzylidenecaniline*:  $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{N} \cdot \text{C}_6\text{H}_5$  may also form mixed crystals with *Stilbene* and *Azobenzene* so that according to them the atomic combination:  $\text{--- CH} = \text{N ---}$  ought to be included in the above series. The question now arises whether the combining forms:  $\text{--- NH---NH---}$  and  $\text{--- CH}_2 \text{--- NH ---}$  which find in *Hydrazobenzene* and *Benzylamine* their most simple representatives, analogous with the above derivatives, belong to this isomorphogenous series or no.

The important question, however, arose whether we have really the right to speak here of an isomorphism, as we are not allowed to conclude at once that an isomorphism exists merely on account of the power of mixing in the solid state only.

BOERIS<sup>3)</sup>, however, demonstrated that the four firstnamed substances exhibit such a close form relationship that this is practically indistinguishable from true isomorphism.

*Dibenzyl*:  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \text{--- CH}_2 \cdot \text{C}_6\text{H}_5$ .

Monoclinic-prismatic  $a : b : c = 2,0806 : 1 : 1,2522$ ;  $\beta = 64^\circ 6'$

*Stilbene*:  $\text{C}_6\text{H}_5 \cdot \text{CH} = \text{CH} \cdot \text{C}_6\text{H}_5$ .

Monoclinic-prismatic  $a : b : c = 2,1701 : 1 : 1,4003$ ;  $\beta = 65^\circ 54'$

*Tolane*:  $\text{C}_6\text{H}_5 \cdot \text{C} \equiv \text{C} \cdot \text{C}_6\text{H}_5$ .

Monoclinic-prismatic  $a : b : c = 2,2108 : 1 : 1,3599$ ;  $\beta = 64^\circ 59'$

*Azobenzene*:  $\text{C}_6\text{H}_5 \cdot \text{N} = \text{N} \cdot \text{C}_6\text{H}_5$ .

Monoclinic-prismatic  $a : b : c = 2,1076 : 1 : 1,3312$ ;  $\beta = 65^\circ 34'$

Here, however, we meet with differences in aspect, optical orien-

<sup>1)</sup> BRUNI and CIAMICIAN, Soluzioni solide e miscele isomorfe fra i composti a catena aperta saturi e non saturi; Rendic. Lincei (1899). 8. I. 575; Gazz. Chimic. Ital. (1899). 29. 149.

<sup>2)</sup> GARELLI and CALZOLARI, Sul comportamento crioscopico di sostanze aventi i costituzione simile a quella del solvente; Rendic. Lincei (1899). 8. I. 585; Gazz. Chim. Ital. (1899). 29. (2). 258; Rendic. Lincei R. Accad. (1900). 9. (1). 382.

<sup>3)</sup> BRUNI and GORNI, Gazz. Chim. Ital. (1899). 1. 55.

<sup>3)</sup> BOERIS, Atti Società Ital. di Sc. Natur., Milano. (1900). 39. 111—123. Abstract Z. f. Kryst. 34. 298.

ation etc. which are greater than is allowed in strictly isomorphous substances, so that it is better to speak of isomorphotropism instead of isomorphism.

Now according to GARFELLI and CALZOLARI, *Dibenzyl* and *Benzyl aniline* form mixed crystals; also *Azobenzene* and *Benzylaniline*<sup>1)</sup>. This in connection with the results previously obtained by MUTHMANN<sup>2)</sup> according to which the *Terephthalic-methyl-ether* is isomorphotropous with  $\Delta_{1,4}$ —, and  $\Delta_{1,3}$ — *Dihydroterephthalic-dimethyl-ether* and the  $\Delta_{1,3}$ — and  $\Delta_{1,5}$ — *Dihydroterephthalic-diethyl-ethers* are isomorphotropous with the  $\Delta_1$ — *Tetrahydroterephthalic-diethyl-ether*, whilst, in addition the *p-Dioxyterephthalic-ethers* behave in an analogous manner to the *p-Dioxydihydroterephthalic-ethers* and are capable of forming with these mixed phases in the solid state, the Italian investigators believe they are justified in coming to the conclusion that *if two aromatic substances can form mixed crystals, their hydro-products can do the same.*

The universal application of this rule is at once upset by *Hydrazobenzene* and *Dibenzyl*, which, cryoscopically, behave quite normally but differ in their crystalline form as shown above.

It was, therefore, to be expected that *Azobenzene* and *Hydrazobenzene* would form no mixed crystals. Experiments taught me indeed that from their mixed solution in ether *Hydrazobenzene* is deposited first in colourless, perfectly pure crystals. Afterwards these are accompanied by pure red crystals of *Azobenzene*; they were verified by the melting point.

I have also determined the melting point line of mixtures of the two substances. This line has two branches and an ordinary eutecticum situated at 59°<sup>25</sup> and corresponding with a concentration in *Azo*-compound of 76.2 mol %.

Here are a few data:

<i>Azobenzene</i>		melts at 67° <sup>8</sup> C.
„ + 9.6 %	<i>Hydrazobenzene</i>	„ „ 63° <sup>4</sup> C.
„ + 17.7 %	„	„ „ 60° <sup>1</sup> C.
„ + 23.8 %	„	„ „ 59° <sup>25</sup> C.
„ + 47.0 %	„	„ „ 84° C.
„ + 70.5 %	„	„ „ 102° <sup>5</sup> C.
<i>Hydrazobenzene</i>		„ „ 125° <sup>2</sup> C.

<sup>1)</sup> BRUNI, Ueber feste Lösungen. Samml. chem. techn. Vorträge. Bd. VI. (1901). p. 48.

<sup>2)</sup> MUTHMANN, Z. f. kryst., 15. 60; 17. 460; 19. 357.

According to my research there is here no question of an isomorphism with an appearing hiatus.

All this is quite in accord with the deviating crystalline form of *Hydrazobenzene*.

It deserves attention that BILLOWS<sup>1)</sup> has investigated *p-Azotoluene* and *p-Hydrazotoluene*. He finds:

*p-Azotoluene* (143° C.)-Monoclinoprismatic

$$a : b : c = 0,5687 : 1 : 1,7105; \beta = 89^{\circ}.44'$$

*p-Hydrazotoluene* (128° C.)-Monoclinoprismatic

$$a : b : c = 0,6279 : 1 : 2,0287; \beta = 89^{\circ}.49'$$

Notwithstanding these deviations, also that one where {001} of the first substance plays the role of {100} at the second he declares these compounds to be "isomorphous"! Of more than a mere morphotropic relation there can be no question here, and the so called isomorphogenous replacement of —N=N— by —NH—NH— does not help us here.

As *Dibenzyl* and *Benzylaniline* can yield mixed crystals and as according to BRUNI the latter yields mixed crystals with *Azobenzene* an analogy in form is to be suspected here. This may indeed be brought to light by assigning to BÖERIS' forms in *Azobenzene*: {100}, {001}, {110}, {201}, {403} respectively the symbols: {100}, {101}, {410}, {101}, {103}, that is to say by calling the form which should be {101} with BÖERIS, {001}.

Then we have:

$$\textit{Azobenzene}: a : b : c = 2,1076 : 1 : 1,4220; \beta = 76^{\circ}.32'$$

$$\textit{Benzylaniline}: a : b : c = 2,1076 : 1 : 1,6422; \beta = 76^{\circ}.36\frac{1}{2}'$$

Therefore, a relation which, having the same ratio *a:b* and an equal angle  $\beta$ , looks as if it ought to be considered as a case of isomorphotropism bordering on isomorphism.

It must, however, be pointed out immediately that this explanation is not a *rational one* as the other forms of *Azobenzene* observed by BÖERIS obtain in this way very complicated symbols.

It must also be observed that the meltingpoint of *Benzylaniline* (36½° C.) is lowered by addition of small quantities of *Azobenzene*.

Whilst the *Benzylaniline* used melted at 36½° C. and the *Azobenzene* at 68° C., the following melting points *t* were found for mixtures:

<sup>1)</sup> BILLOWS, Rivista di Mineral. e Cristall. Ital. (1903). 30. 34—48. Abstract Z. f. Kryst. 41. 273.

93½ %	<i>Benzylaniline</i>	+	6½ %	<i>Azobenzene</i> ,	$t = 35^\circ \text{C.}$
88 %	"		12 %	"	$t = 32\frac{1}{2}^\circ \text{C.}$
48,6%	"		51,4%	"	$t = 49^\circ \text{C.}$
23,7%	"		76,3%	"	$t = 61\frac{1}{2}^\circ \text{C.}$

On crystallisation of the two compounds from a joint solution in alcohol + chloroform, small aggregated orange-coloured needles were obtained which were unsuitable for further investigation. But it seems that solid solutions are formed here.

As regards *Azobenzene* and *Stilbene* with which *Dibenzyl* forms solid solutions, I have tried to determine, in mixtures of the two substances, the points of initial and final solidification in the usual manner. It appeared that these two substances whose isomorphotropism is almost indistinguishable from real isomorphism, also agree with real isomorphous substances in this respect that they can form a continuous series of mixed phases from 0 % to 100 %. The lower branch of the continuously-rising melting point curve is situated so close to the higher one that a sharp determination was quite impossible.

The following melting points were found:

*Azobenzene* melts at  $68^\circ \text{C.}$

" + 22,9 % *Stilbene* melts at  $82^\circ.4 \text{C.}$

" + 66,94% " " "  $107^\circ.2 \text{C.}$

*Stilbene* melts at  $120^\circ \text{C.}$

The melting point of *Azobenzene* is therefore raised by addition of *Stilbene*. The lowering of the melting point of *Stilbene* is not proportional to the number of molecules of added *Azobenzene* (incorrect rule of KÜSTER) but takes place more slowly.

The mixed crystals obtained from mixed solutions were homogeneous and of a bright red colour. They crystallise beautifully. The mixture being sublimed the vapour deposits mixed crystals as is also observed by BRUNI.

Finally, we wish to observe that *Hydrazobenzene*, notwithstanding the difference in symmetry, shows in its parameters some degree of analogy with *Azobenzene* if we take  $o = \{211\}$ ,  $\omega = \{421\}$  and  $m = \{210\}$ .

*Azobenzene*:  $a : b : c = 2,1076 : 1 : 1,4220$   $\beta = 76^\circ.32'$ .

*Hydrazobenzene*:  $a : b : c = 1,9574 : 1 : 1,2497$   $\beta = 90^\circ$ .

In the case of *Diphenylhydrazine*, notwithstanding its great similarity to the monoclinic system, there is no question of such a distant analogy.

**Chemistry.** — "*The amides of  $\alpha$  and  $\beta$ -aminopropionic acid.*". By Prof. A. P. N. FRANCHIMONT and Dr. H. FRIEDMANN.

(Communicated in the meeting of October 28, 1905).

Some time ago, I was asked for information as to a substance isolated in 1873 by BAUMSTARK from some urines. He describes it as white prisms some millimetres long and resembling hippuric acid not only in form but also in lustre. It is fairly readily soluble in boiling water, with difficulty in cold water and spirit of wine, insoluble in absolute alcohol and ether, and suffers no decomposition when heated to  $250^\circ$ . It is a neutral substance which, however, yields with acids, hygroscopic compounds difficult to crystallise, and gives a precipitate with mercuric nitrate. The analysis led to the formula  $\text{C}_8\text{H}_8\text{O N}_2$ . By means of nitrous acid he obtained from it a liquid acid and from this he prepared a zinc salt, which in zinc and water content corresponds with the zinc salt of sarcosolactic acid. This zinc salt was very soluble in water and in spirit of wine, and from this he concluded that it really consisted of zinc sarcosylactate. He also showed that under the influence of alkalis, one nitrogen atom is readily converted into ammonia and the other into ethylamine, carbon dioxide being also formed.

From this he concluded that his substance was the amide of  $\alpha$ -aminopropionic acid or, as he called it, the diamide of lactic acid.

BELSTEIN in his text-book, mentions BAUMSTARK's substance as the amide of  $\alpha$ -aminopropionic acid but adds a point of interrogation, and rightly so, for BAUMSTARK has tried to control the conclusion drawn from his analytical research by synthetically preparing the diamides of the lactic acids, or amides of the amino-propionic acids, and comparing them with his substance from the urine; from those experiments he drew the opposite conclusion, and declared the previous idea to be incorrect.

But if we look at the synthetical methods applied by BAUMSTARK, it is at once evident that he could obtain nothing else but mixtures, which he has not separated but seems to have regarded as pure substances whose properties were totally different from that of his substance from urine.

Moreover, many, particularly physical properties such as melting point, solubility, neutrality etc. of the substance from urine, are not those which we might reasonably expect of the amides of the amino-propionic acids.

None of the amides of the aminopropionic acids being known, I