

*Citation:*

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In the system of the carvoxims it is sure to be the same case and then the equation of the three-phase line becomes

$$T \frac{dP}{dT} = \frac{Q_{GS} - Q_{LS}}{V_{GS} - V_{LS}} = \frac{Q_{GL}}{V_{GL}}$$

The three-phase line simply coincides with the vapour tension line for liquid carvoxim (whether *d*, *l*, *r* or a mixture) between the melting temperature of the components and that of the pseudo-racemic mixed crystal. This curve is then a double line and in a certain sense we might then say that it has one maximum which of course, is plainly noticed in the *Px*-projection.

But as to the decision between racemic compounds and pseudo-racemic mixed crystals this course of the three-phase line yields no criterion. Only, VAN LAAR <sup>1)</sup> has pleaded for the conception that the form of the melting line of the carvoxims solely points to a compound, whereas TAMMANN <sup>2)</sup> on account of caloric values exactly arrives at the opposite result.

Utrecht, August 1916.

VAN 'T HOFF-Laboratory.

**Chemistry.** — “On Nitro-derivatives of Alkyltoluidines and the relation between their molecular refractions and those of similar compounds”. By Dr. J. D. JANSEN. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of June 24, 1916).

Some years ago appeared a communication from HANTZSCH <sup>3)</sup> on chromoisomerism and homochromoisomerism of nitroanilines. In the conclusion of this remarkable publication, HANTZSCH says that yellow and orange di- and tri-nitroanilines, when their molecular refractions are abnormal, probably contain chromophores of different constitution. The *yellow* 3.4. dinitro-dimethyl-aniline and the *orange* 3.4. dinitro-diethyl-aniline, according to his opinion, are not *real*, but *pseudo*-homologues, which manifested itself in the molecular refractions,

$$mRTl \frac{x_G}{1 - x_G} = mRTl \frac{x_L}{1 - x_L}$$

or

$$x_G = x_L$$

The fact that  $a_{12} = a_1$  certainly points out that in the liquid and vapour occur no (or at least *very* few) racemic molecules.

<sup>1)</sup> Zeitschr. f. physik. Chem. **64**, 289 (1908).

<sup>2)</sup> Göttinger Nachrichten 1913.

<sup>3)</sup> B **43**, 1662, (1910).

which did not differ double the refractive effect calculated by BRÜHL for the  $\text{CH}_2$  group viz. 9.2, but only 7.8.

In order to indicate the difference between those pseudo-homologues HANTZSCH avails himself of subsidiary valencies.

As HANTZSCH stated he had obtained the 3.4. dinitro-dimethyl-aniline by the action of nitric acid (D. 1,3) on dimethylaniline, v. ROMBURGH<sup>1)</sup> supposed that for his experiments he did not use this substance, but 2.4. dinitro-*mono*-methyl-aniline. This supposition proved to be true, as indeed in the above mentioned reaction this substance was formed.

In connection with this mistake it appeared to me of some interest to test the theory of HANTZSCH, built by him on the investigation of these two and five more substances, to a far more extensive material. At the same time I wish to combine with this research an investigation concerning the nitration of dimethyl- and diethyl-*p*-toluidine, because in doing this I expected to obtain different substances, which with a great number of conformable nitroanilines, kindly put to my disposition by Prof. v. ROMBURGH, I might subject to a comparative refractometric research.

#### *Nitro-derivatives of dimethyl-p-toluidine.*

I prepared dimethyl-*p*-toluidine according to the method of STADEL<sup>2)</sup>. After having converted this, by nitration in conc. sulfuric acid, into 2. nitro-dimethyl-*p*-toluidine, I tried to nitrate this last substance further with diluted nitric acid.

To this end, I dissolved 3 grams of this product in 40 c.c. of nitric acid (D. 1,20) and added some sodium nitrite. Soon a pale yellow substance precipitated, showing the composition of a dinitro-tolyl-methyl-nitrosamine, which however proved to be a mixture of 2.3- and 2.5-dinitro-tolyl-methyl-nitrosamine. To prevent the formation of nitrosamines I decided to add urea.

7.5 Grams of 2 nitro-dimethyl-*p*-toluidine were added in little portions to 150 c.c. of nitric acid (D. 1,20) in which 0.5 gram of urea had been dissolved. Next day, the brownish-red liquid, which did not deposit a precipitate, is cautiously mixed with water. When about 150 c.c. had been added, an orange-brown substance began to separate slowly. This having been deposited, water was slowly

<sup>1)</sup> Proc. Roy. Akad. Amst. Jan. 28, 1911.

<sup>2)</sup> B. 16, 29 (1883). If HBr-*p*-toluidine is heated with a surplus of methyl alcohol, then is produced as a bye-product the trimethyl-*p*-tolylammoniumbromide, beautiful colourless crystals, which decompose at about 225°.

added again and once more the solution gave a quantity of the same substance. On adding water to the filtrate this at first remained clear, but when about 150 c.c. had been added, a red substance precipitated. By the addition of more water, some more of this substance was obtained, while at last by neutralisation with soda a small quantity of the original product separated.

The red substance melted at  $103^{\circ}$  and appeared to be the already known 2,5-dinitro-dimethyl-p-toluidine. The orange brown substance, fairly soluble in boiling alcohol, melted at  $87^{\circ}$ . Seeing the analytical results I supposed I had to do with the still unknown 2,3-dinitro-dimethyl-p-toluidine. This proved to be the case indeed, as by oxidation with chromic acid it is converted into 2,3-dinitro-monomethyl-p-toluidine, described by PINNOW <sup>1)</sup>.

I also converted the 2,3-dinitro-dimethyl-p-toluidine into the 2,3-dinitro-tolyl-methyl-nitrosamine, by dissolving it in nitric acid (D 1.20) and by slowly adding sodium nitrite. The nitrosamine precipitated, which on being boiled with acetic acid changed into the 2,3-dinitro-methyl-p-toluidine melting at  $159^{\circ}$ .

If the 2,3-dinitro-dimethyl-p-toluidine is boiled for some time with ten parts of nitric acid (D. 1.49), then on pouring it out into water the already known 2,3,5 trinitro-4-tolyl-methyl-nitramine (m. p.  $157^{\circ}$ ) precipitates.

As the 2,3-dinitro-dimethyl-p-toluidine contained two nitro-groups in ortho-position, I thought it might be of some interest to try to substitute one of them by interaction of ammonia and of different amines. For in this way, the ortho-position of the nitro-groups might be defined in another way than had been done by PINNOW (l. c.); at the same time might appear the degree of mobility of that nitro-group which was to be substituted.

It was to be expected, that the substitution of the nitro-group would not be easy. SOMMER <sup>2)</sup> had studied the action of ammonia and of different amines — aliphatic as well as aromatic — on 2,3,5-trinitro-methyl-p-toluidine and on the nitrosamine and nitramine derived from it and he had experienced that it is true that the nitro-group was substituted, whilst methylamine also acted on the nitramino-group, but that it was necessary in case of ammonia, methyl- and dimethyl-amine to work at  $100^{\circ}$  under pressure.

Therefore I heated 0.5 gram of 2,3 dinitro-dimethyl-p-toluidine with 5 c.c. of alcohol and 5 c.c. of ammonia (D. 0.91) for some

<sup>1)</sup> J. p. Chem. **62**, 505 (1900).

<sup>2)</sup> J. p. Chem. **67**, 513 (1903).

hours in a press bottle in a water-bath. After cooling, the original compound crystallized. Also after heating with alcoholic solutions of methyl-, dimethyl- and ethyl-amine I could not state that the nitro-group had been acted upon.

Aniline also, which does act on the 2.3.5-trinitro-methyl-p-toluidine, did not act on the 2.3-dinitro-dimethyl-p-toluidine. Nor could amines act on the nitro-group of the 2.3 dinitro-mono-methyl-p-toluidine.

Thus the nitro-group (2) proves to be very closely united with the nucleus. SOMMER supposed this difficult substitution to be caused by "steric hindrance" by the neighbouring methyl-group.

In order to examine this I heated 0.5 gram of 2.3-dinitro-aniline with 5 c.c. of alcohol and 5 c.c. of ammonia (D. 0.91) for one hour in a press bottle in a water-bath. The compound proved unchanged.

From all those experiments it appears again that to define the structure, the rule of LAUBENHEIMER is only to be used with great reserve.

#### *Nitro-derivatives of diethyl-p-toluidine.*

I got 2-nitro-diethyl-p-toluidine according to ALFTHAN's method <sup>1)</sup>. If the nitrating liquid is poured out into a large quantity of iced water, so that the temperature remains below 25°, then nothing else separates but the mono-nitro-product, a red oil (b. p. 195° at 17 m.m.), even when a large surplus of nitric acid has been used. ALFTHAN, who also obtained higher nitrated products by this reaction, evidently had not kept the temperature low while pouring out into iced water.

When 2-nitro-diethyl-p-toluidine is boiled for some time with conc. nitric acid, then it changes into 2.3.5-trinitro-tolyl-ethyl-nitramine (m. p. 98°), a light yellow substance already described by ALFTHAN.

More easily is this nitramine to be obtained by nitrating mono-ethyl-p-toluidine, dissolved in conc. sulphuric acid at low temperature with a large quantity of conc. nitric acid <sup>2)</sup>.

While keeping the temperature below 0° I dropped 8 c.c. of nitric acid (D. 1.49) dissolved in 20 c.c. of sulphuric acid into 10 c.c. of ethyl-p-toluidinê dissolved in 110 c.c. of the same acid (D. 1.84). After some time I slowly added 100 c.c. of nitric acid (D. 1.49) — continually cooling the mass — and then left the liquid in a basin of water till next day. On pouring it out into ice the 2.3.5-trinitro-tolyl-ethyl-nitramine precipitated.

When this substance is boiled for six hours with phenol, amyl

<sup>1)</sup> Thèse, Genève (1909).

<sup>2)</sup> VAN ROMBURGH & SCHEPERS, Proc. Roy. Akad. Amst. 369 (1913).

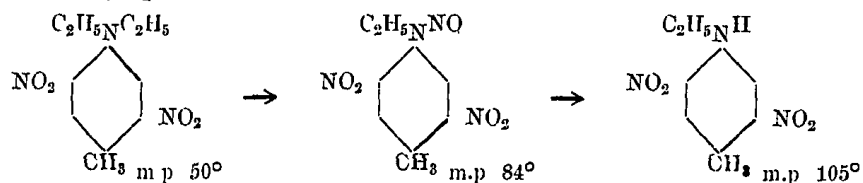
alcohol and some drops of conc sulphuric acid <sup>1)</sup>, then 2.3.5-trinitro-ethyl-p-toluidine, a yellow compound (m.p. 150°), is formed.

On nitrating diethyl-p-toluidine, dissolved in conc. sulphuric acid, with a quantity of nitric acid calculated for two nitro-groups and on afterwards pouring it out into four volumes of water, the temperature rising to about 50°, the red 2.5-dinitro-diethyl-p-toluidine is formed (m.p. 50°) the structure of which has been defined by ALFTHAN. However, if I poured it out into two volumes of water, the temperature now rising to 80°. a cloudiness with evolution of nitrous vapours suddenly manifested itself. A light red crystalline mass was slowly formed. This mass was treated with hydrochloric acid (D. 1,19); part of it dissolved and by dilution a red precipitation, the 2.5-dinitro-ethyl-p-toluidine (m.p. 105°), was formed in this solution.

That part which did not dissolve in hydrochloric acid was recrystallized from acetone and afterwards from alcohol and formed a light yellow compound, 2.5-dinitro-tolyl-ethyl-nitrosamine (m.p. 84°).

I could prove that the nitro-groups of the last mentioned compounds really take the places 2 and 5 by nitrosating the 2.5-dinitro-diethyl-p-toluidine.

On dissolving this substance in nitric acid (D. 1.2) and slowly adding sodium nitrite the above described nitrosamine (m. p. 84°) precipitates, which changes by boiling with acetic acid into the red 2.5-dinitro-ethyl-p-toluidine (m. p. 105°).



If the three above mentioned substances are boiled with nitric acid (D. 1.49), they change into the 2.3.5. trinitro-tolyl-ethyl-nitramine.

#### *Nitro-derivatives of ethyl-o-toluidine.*

I started from 4-nitro-ethyl-o-toluidine prepared by nitrating ethyl-o-toluidine in twenty times its weight of sulfuric acid. Like HANTZSCH <sup>2)</sup> I obtained it in *yellow* crystals and not as MAC CALLUM <sup>3)</sup> mentions in *light red* needles.

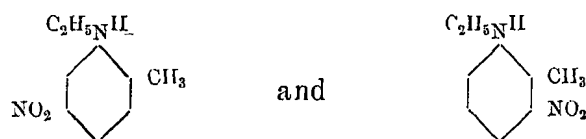
The latter reduced the nitro-group and got from the diamine, which had been formed, a chrysoidine by means of diazobenzene

<sup>1)</sup> SOMMER, J. p. Chem. **67**, 535 (1903).

<sup>2)</sup> B **43**, 1673 (1910).

<sup>3)</sup> J. Chem. Soc. **67**, 246 (1895).

chloride, thus proving the meta-position of the nitro- in relation to the amino-group. He assigned to the nitro-group place 4, though as a consequence of his research two structure-formulae were possible:

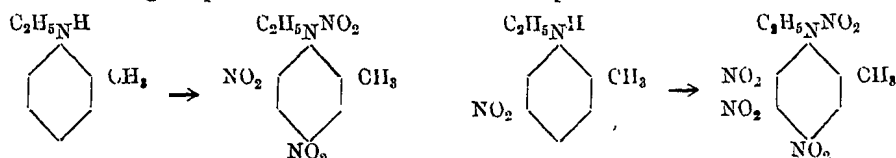


In order to prove that the first formula is the right one I ethylated 4-nitro-o-toluidine and got a yellow compound, identical with the nitro-ethyl-o-toluidine described above.

When the 4-nitro-ethyl-o-toluidine is boiled during some time with nitric acid (D. 1.49) an almost colourless compound (m. p. 112—113°) is formed, the analysis of which proves it to be a trinitro-o-tolyl-ethyl-nitramine.

The same substance is formed by nitrating ethyl-o-toluidine dissolved in conc. sulfuric acid with a large surplus of conc. nitric acid in the same way as described for the ethyl-p-toluidine. On pouring the liquid out on ice, which after having been left for one day, had become turbid by fine oil-like drops contained in it, the trinitro-o-tolyl-ethyl-nitramine precipitated. However if I left the liquid alone for several days, in some cases a crystalline mass was deposited therein, which proved to consist of the same almost colourless crystals.

As the ethyl-o-toluidine by nitration with nitric acid (D. 1.49) changes into the 3.5. dinitro-o-tolyl-ethyl-nitramine <sup>1)</sup> we must assign to the nitro-groups of the new nitramine places 3, 4, and 5.



When the nitramine is boiled for some hours with phenol, amyl-alcohol and some drops of conc. sulphuric acid, the 3.4.5. trinitro-ethyl-o-toluidine is formed, which recrystallized from alcohol produces yellow needles melting at 150°.

#### *Refractometric determinations.*

After having dissolved the nitrocompounds in pyridine, the refractive indices for sodium light were measured with the refractometer of PULFRICH "Neuconstruction". Here follow some of the molecular refractions (M.-R.) measured by me <sup>2)</sup>. The corresponding numbers

<sup>1)</sup> v. ROMBURGH. Rec. **3**, 402 (1884).

<sup>2)</sup> I have used the formula of LORENTZ LORENZ.

in the second list have been found by HANTZSCH; they refer to compounds of the *same* colour.

	M.-R.	$\Delta$	M.-R.	$\Delta$
2.4. dinitro-aniline . . . . .	50,4			
2.4. dinitro-methyl-aniline . . . . .	56,2			
2.4. dinitro-ethyl-aniline . . . . .	61,2			
2.4. dinitro-dimethyl-aniline . . . . .	61,1	9,4	62,2	9,5
2.4. dinitro-diethyl-aniline . . . . .	70,5	9,8	71,7	9,4
2.4. dinitro-dipropyl-aniline . . . . .	80,3		81,1	

The values found by me are somewhat smaller than those found by HANTZSCH. He used chloroform as a solvent, I used pyridine. The differences between the homologous members (indicated by  $\Delta$ ) are alike in the two series, if we take into consideration that the experimental errors become considerable in consequence of the high molecular weights. It is to be remarked that the molecular refractions of the dimethyl- and the ethyl-compound are the same.

We shall now pass on to the comparison of the other determinations by HANTZSCH with mine, the latter being placed in the first row.

	M.-R.	$\Delta$	M.-R.	$\Delta$
3.4. dinitro-dimethyl-aniline (yellow) . . . . .	62,8	10,3	61,5	7,8
„ „ diethyl-aniline (orange) . . . . .	73,1		69,3	
2.4.6. trinitro-dimethyl-aniline (y.) . . . . .	65,7	9,3	63,1	8,1
„ „ diethyl-aniline (o.) . . . . .	75,0	9,6	71,2	
„ „ dipropyl-aniline (o.) . . . . .	84,6			

The results are very different for these homologues, which have *not* got the *same* colour. This is easy to explain for the 3.4. dinitro-dimethyl-aniline, because HANTZSCH did not use *this* substance, but the 2.4. dinitro-mono-methyl-aniline.

Except the already mentioned nitro-compounds I have still examined other homologues of the same as well as of different colours. For convenience' sake, I unite them all in two groups. First those having the same colour (yellow, orange, or red) and under them, those differing in colour.

	M.-R.	M.-R.	$\Delta$
m-nitro-dimethyl- <i>and</i> -diethyl-aniline (o.) . . . . .	48,5 and 58,2		9,7
p-nitro-dimethyl- <i>and</i> -diethyl-aniline (y.) . . . . .	56,6 „ 67,2		10,6
2.4. dinitro-dimethyl- <i>and</i> -diethyl-aniline (y.) . . . . .	61,1 „ 70,5		9,4
3.6. dinitro-dimethyl- <i>and</i> -diethyl-aniline (r.) . . . . .	56,8 „ 65,3		8,5



	M.-R.	M.-R.	$\Delta$
2 nitro-dimethyl- <i>and</i> -diethyl-toluidine (o.) . . .	53,1	and 62,1	9,0
2.5. dinitro-dimethyl- <i>and</i> -diethyl-toluidine (r.) .	61,4	„ 69,2	7,8
3.4. dinitro-dimethyl- (y.) <i>and</i> -diethyl-aniline (o.)	62,8	„ 73,1	10,3
2.4.6. trinitro-dimethyl- (y.) <i>and</i> -diethyl-aniline (o.)	65,7	„ 75,0	9,3
3.4.6. trinitro-dimethyl- (o.) <i>and</i> diethyl-aniline (y.)	68,2	„ 77,5	9,3

From these determinations it is clear that both with the homologues having the same colour and with those having different colours, the difference of the molecular refractions is sometimes far removed from that calculated by BRUHL (4,6 per CH<sub>2</sub> group).

Therefore in my opinion the refractometric determinations do not make me assume from the difference in colour of homologues that there is a difference in their subsidiary valencies.

This consideration caused me to carry on my research of molecular refractions in quite another direction.

Some years ago HANTZSCH<sup>1)</sup> had called attention to the fact that with the nitro- and aldehydephenols, as well as with their salts and also with the nitroanilines the orthocompounds have smaller molecular-refraction than the para ones.

Now I intended not only to test a number of mononitroanilines by the rule given by HANTZSCH, but also to seek among several aromatic nitro-compounds relations between the value of the molecular refraction, and the position of the groups united with the benzene-nucleus.

If really these relations existed, then for nitro-compounds the refractometer might be used as a welcome instrument to define their constitution.

The relation as stated by HANTZSCH between the value of the molecular refraction and the position of the nitro-group I could observe with a number of compounds.

	M.-R.	$\Delta$	M.-R.	$\Delta$
p-nitro-aniline . . . . .	44,8	3,5	45,36	3,40
o-nitro-aniline . . . . .	41,3		41,96	
m-nitro-aniline . . . . .	38,7			

The numbers I found in pyridine-solution are somewhat lower than those found by HANTZSCH, who dissolved in acetone; however the differences are the same.

<sup>1)</sup> B. 43, 100 and 1656 (1910).

The same order ( $p > o > m$ ) exists with the nitro-dimethyl- and diethyl-anilines and also in the nitro-toluidines.

	M-R.	M-R.
p-nitro-dimethyl- <i>and</i> -diethyl-aniline . . . . .	56,6	67,2
o-nitro-dimethyl-aniline . . . . .	48,9	
m-nitro-dimethyl- <i>and</i> -diethyl-aniline. . . . .	48,5	58,2
3. nitro-p-toluidine . . . . .	M-R. = 46,7	
2. nitro-p-toluidine . . . . .	M-R. = 43,2	

Relation between constitution and molecular-refraction proved to exist not only with the mono-nitro-anilines (toluidines), but also with those anilines (toluidines) which contained more than *one* nitro-group.

For instance: of the 3.4-, 2.4- and 3.6-dinitro-dimethyl (diethyl)-anilines, the first possessed the largest, the last the smallest molecular-refraction.

	M-R.	M-R.
3.4-dinitro-dimethyl- <i>and</i> -diethyl-aniline . . . . .	62,8	73,1
2.4 " " " " " . . . . .	61,1	70,5
3.6 " " " " " . . . . .	56,8	65,3

The same order ( $2.4 > 3.6$ ) exists with the methyl and ethyl-derivatives.

2.4-dinitro-methyl- <i>and</i> -ethyl-aniline . . . . .	56,2	61,2
3.6. " " " " " . . . . .	54,9	59,6

With the dinitro-p-toluidines the position 2.5 gives larger molecular refraction than 2.3.

2.5-dinitro-methyl- <i>and</i> -dimethyl-toluidine . . . . .	60,2	61,4
2.3- " " " " " . . . . .	58,2	59,6

The irregular behaviour of the 3.5- and 2.6-dinitro-toluidines must be mentioned here, because it contrasts with these regularities.

3.5-dinitro-toluidine and 3.5-dinitro-dimethyl-toluidine . . . . .	55,0	58,8
2.6- " " " 2.6- " " " . . . . .	49,6	59,8

With the trinitro-dimethyl (diethyl)-anilines I examined, the compounds with the nitro-groups in the position 3.4.6 showed larger molecular refraction than in 2.4.6.

3.4.6-trinitro-dimethyl- <i>and</i> -diethyl-aniline . . . . .	68,2	77,5
2.4.6- " " " " " . . . . .	65,7	75,0

On the strength of these determinations we may state that the molecular refraction of nitrated anilines and toluidines depends to a high degree on the position of the nitro-groups with respect to the amino-group.

Contrasting with these great *differences* in molecular refractions of isomeric nitro-anilines, we find that those of dinitro-benzenes and nitro-toluenes are practically *the same*.

1.4	Dinitro-benzene.	M-R. = 39,2	1.4.	Nitro-toluene.	M-R. = 38,1
1.2	„ „ „	= 38,8	1.2.	„ „ „	= 37,4
1.3	„ „ „	= 38,8	1.3	„ „ „	= 37,6

The explanation of this difference in properties between the two last-mentioned groups and the nitro-anilines and -toluidines is possible, when we take into consideration the light-absorption.

The absorptioncurves of several substances I used are known. All the nitro-anilines and nitro-toluidines have an absorption band — sometimes a very deep one — near the visible part of the spectrum, whereas in the dinitro-benzenes and nitro-toluenes this band has either disappeared or is situated a long way off, in the ultraviolet.

As an example may serve ( $\lambda$  in Ångstrom-units):

o-Nitro-aniline. <sup>1)</sup> Shows a deep band ( $\lambda \pm 4080$ ) and a shallow one ( $\lambda \pm 2800$ ).

m-Nitro-aniline. <sup>2)</sup> Shows a band ( $\lambda \pm 3700$ ).

p-Nitro-aniline. <sup>2)</sup> Shows a very deep band ( $\lambda \pm 3840$ ).

The molecular refractions of these compounds are, as has already been stated, very different.

o-Nitro-toluene. <sup>3)</sup> Shows a band ( $\lambda \pm 2450$ ).

m-Nitro-toluene. <sup>3)</sup> „ „ „ ( $\lambda \pm 2630$ ).

p-Nitro-toluene. <sup>3)</sup> „ „ „ ( $\lambda \pm 2780$ ).

The molecular refractions are almost equal.

o-Dinitro-benzene. <sup>4)</sup> Shows no band between  $\lambda 4000$  and  $\lambda 2000$ .

m-Dinitro-benzene <sup>4)</sup> Shows no band.

p-Dinitro-benzene. <sup>4)</sup> Shows a band ( $\lambda \pm 2560$ ).

Also with the following, nearly *colourless*, compounds having no absorptionband in the visible part of the spectrum, the isomerides have almost *similar* molecular refraction.

o-Xylene <sup>5)</sup>	M-R. = 35,74	o-Toluidine <sup>5)</sup>	M-R. = 35,33
m-Xylene	„ 35,90	m-Toluidine	„ 35,33
p-Xylene	„ 35,95	p-Toluidine	„ 35,95

<sup>1)</sup> PURVIS and MC. CLELLAND. J. Chem. Soc. **103**, 1104 (1913).

<sup>2)</sup> DALY, TUCK and MARSDEN, „ „ „ **97**, 582 (1910).

<sup>3)</sup> „ „ „ „ „ „ „ 572 „

<sup>4)</sup> PURVIS and MC. CLELLAND, „ „ „ **103**, 1100 (1913).

<sup>5)</sup> LANDOLT BORNSTEIN p 1032 and 1033 (1912).

o-Cresol <sup>1)</sup>	M-R <sub>z</sub> = 32,52	o-Chloraniline <sup>2)</sup>	M-R. = 35,46
m-Cresol	„ 32,56	m-Chloraniline	„ 35,55
p-Cresol	„ 32,57		

The molecular refractions of isomeric compounds are almost the same, if the absorption bands are situated far outside the visible part of the spectrum.

If however these bands are situated very near to or in the visible part of the spectrum, as is the case with all nitro-anilines and -toluidines examined so far, then the molecular refractions show great differences.

So it is evident that in the last mentioned substances the value of the molecular-refraction depends on the presence of absorption bands in the neighbourhood of the kind of light chosen for the determination of the refraction

In connection with this we call attention to the molecular refractions of the 2.3- and 2.5-dinitro-dimethyl-p-toluidine and the respective nitrosamines.

2.3. Dinitro-dimethyl-p-toluidine.	M-R. = 59,6	} $\Delta = 1,8$
2.5. „ „ „ „	„ 61,4	
2.3. Dinitro-tolyl-methyl-nitrosamine.	„ 56,9	} $\Delta = 0,5$
2.5. „ „ „ „	„ 57,4	

The difference in molecular refraction of the two strongly coloured dinitro-dimethyl-p-toluidines has almost disappeared, after substitution of a NO-group for a CH<sub>3</sub> group, in consequence of which almost colourless nitrosamines are formed.

Besides the molecular refractions of these nitrosamines are much smaller than those of the dimethyl compounds.

A careful examination of the molecular-refraction and absorption curve brings the following relations to light.

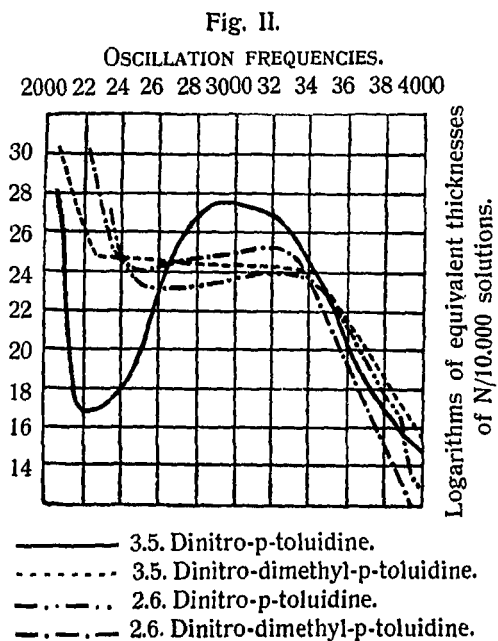
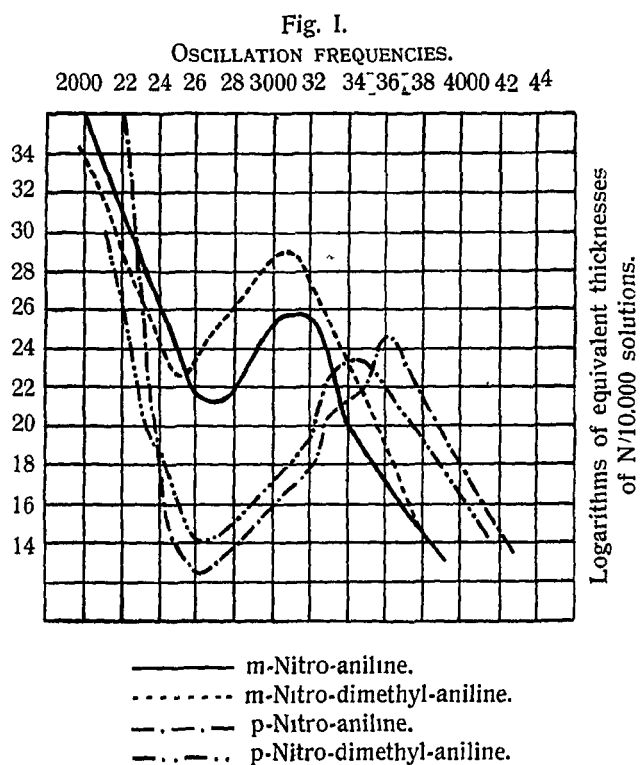
As has already been observed the molecular refraction is to a high degree dependent on the position of the nitro-group with respect to the amino-group. If we arrange isomerides according to the value of their molecular refractions and if we act in like manner with the homologues of these isomerides, then in both cases we get the same succession save a single exception which is easy to explain. Thus we have:

M.-R. of p-nitro-aniline	>	M.-R. of m-nitro-aniline.
M.-R. of p-nitro-dimethyl-aniline	>	M.-R. of m-nitro-dimethyl-aniline.

<sup>1)</sup> EYKMAN, Rec. 12, 177 (1893).

<sup>2)</sup> See note 5 p. 573

This phenomenon is to be explained by observing the absorption curves (fig. I)<sup>1)</sup>, the curves of the two para-derivatives, which are



<sup>1)</sup> Baly, Tuck, and Marsden, J. Chem. Soc. 97, 582 (1910).

nearly similar, vary greatly from the curves of the two meta-derivatives, which are also nearly similar.

The molecular refraction of the p-nitro-aniline, the absorption band of which is much deeper and lies nearer to the yellow, is larger than that of the m-nitro-aniline.

The 3.5- and 2.6-dinitro-p-toluidines and their dimethyl-derivatives behave very irregularly. Here we have an example of the above mentioned exception.

	M.R.	M.R. $\Delta$	
3.5-dinitro-toluidine and 3.5-dinitro-dimethyl-toluidine	55,0 and 58,8	3,8	
2.6. „ „ „ 2.6. „ „ „	49,6 „ 59,8	10,2	

A look at the absorption curves (fig. II)<sup>1)</sup> explains this behaviour. The curves of the two 2.6-dinitro-derivatives are almost similar, whereas those of the 3.5-dinitro-compounds diverge greatly. The molecular refraction of the 3.5-dinitro-p-toluidine, which possesses a deep absorption band, differs very little from that of its dimethyl derivative (3,8); this is in perfect accordance with the well-known fact that on the red side of a deep absorption band the refractive index is raised (anomalous dispersion).

Utrecht.

Org. Chem. Univ. Lab.

**Physics.** — “On adiabatic changes of a system in connection with the quantum theory.” By Prof. Dr. P. EHRENFEST. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 24, 1916).

*Introduction.* In an increasing number of physical problems the foundations of classical mechanics (and electrodynamics) are used together with the quantum hypothesis, which is in contradiction with them. It remains of course desirable to come here to some general point of view from which each time the limit between the “classic” and the “quantum” region may be drawn.

WIEN’s law has been found by an application of classic principles: the changes of the distribution of the energy over the spectrum and the work done by a reversible adiabatic compression are calculated quite according to classic electrodynamics. This law derived without the use of quanta stands unshaken amid the quantum theory. This fact now is worth our attention.

Perhaps something similar holds in more general cases, when no longer harmonic vibrations take place, but more general motions:

<sup>1)</sup> MORGAN, JOBLING, and BARNETT, J. Chem. Soc. **101**, 1211 (1912).