

weight, a result which would agree with Landolt's elaborate study of the question.<sup>1</sup> It is hoped that this problem may be taken up again by a method capable of giving more accurate results.

BUREAU OF STANDARDS,  
Washington, August, 1907.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY No. 147].

## THE STEREOCHEMISTRY OF INDIGO. PRELIMINARY COMMUNICATION.

BY K. GEORGE FALK AND J. M. NELSON.

Received September 28, 1907.

Organic compounds which contain a double bond are capable in general, of existing in two geometrical-isomeric forms. The following lists include a number of these compounds of which one or both of the isomers are colored.

*Double bond between two carbon atoms* ( $>C=C<$ ). (When the spacial relations were not given with this group of compounds, the lower melting form was assigned the *cis* structure).

Substance	<i>Cis</i> Form		<i>Trans</i> Form	
	M.P.	Color	M.P.	Color
Dibenzoyl ethylene <sup>2</sup>	111°	intense yellow	134°	colorless
Diethoxynaphthostilbene <sup>3</sup>	185-186°	yellow	...	"
Benzaldesoxybenzoin <sup>4</sup>	88-89°	yellow	101-102°	"
Diphenyldinitroethylene <sup>5</sup>	105-106°	yellow	186°	deeper yellow
Piperonylacrylic acid methyl ester <sup>6</sup>	107°	yellow	111°	almost white
$\alpha$ -Benzal- $\gamma$ -diphenylitaconic acid <sup>7</sup>	...	yellow	...	colorless
" " anhydride <sup>7</sup>	218°	red	267°	"
Dibenzalsuccinic acid <sup>7</sup>	218°	yellow	254°	"
" " anhydride <sup>7</sup>	263°	yellow	...	"
Oxidation product of $\beta$ -benzoylpropionic acid <sup>7</sup>	sublimes	red	sublimes	yellow

The general conclusion to be drawn from the accompanying tables is that if a compound exists in two geometrical isomeric forms and one of these isomers is colored, the other isomer will either be colorless or possess a different color from the first. For the special classes of compounds considered, the following relations may be deduced:—

For compounds containing a double bond between two carbon atoms the *cis* forms are more deeply colored.

For oximes, the *anti* forms have higher melting points, are more deeply colored and less soluble.

For hydrazones the *anti* ( $\alpha$ ) forms have lower melting points, are more deeply colored, and more soluble.

For diazosulphonates, the *syn* forms are more deeply colored.

<sup>1</sup> Z. physik. Chem., 55, 589.

<sup>2</sup> Ber., 33, 3795; 35, 168. <sup>3</sup> J. pr. Chem., 47, 72. <sup>4</sup> Ber., 34, 3897.

<sup>5</sup> Ibid., 34, 619. <sup>6</sup> Ibid., 24, 618. <sup>7</sup> Werner "Stereochemie", p. 214.

OXIMES		Syn	R.C.H    N.OR'	Color	Solubility	M.P.	Anti	R.C.H    R'IO.N Color	Solubility
Quinone dioxime <sup>1</sup>				Light grey				Yellow	
“ “ diacetate <sup>1</sup>	147°				more	190°			less
<i>m</i> -Nitrobenzaldoxime sodium <sup>2</sup>				Light yellow				yellow	
4-Chlortoluquinone oxime <sup>3</sup>	165°			“ “	easily	170°		brownish yellow	difficultly
Acetyl “ “ “ <sup>3</sup>	141-142°			“ “	“	158-159°		amber yellow	“
4-Brontoluquinone oxime <sup>3</sup>	178-180°			“ “	“	186°		brownish yellow	“
Acetyl “ “ “ <sup>3</sup>	131-132°			“ “	“	166-167°		amber yellow	“

	Syn-β- R'H.N.N			Anti-α- R.C.Ac    N.NHR'		
	M.P.	Color	Solubility	M.P.	Color	Solubility
Benzaldehydephenylhydrazone <sup>4</sup>	136°	white	.....	152°	almost colorless	....
Nitroformaldehydephenylhydrazone <sup>5</sup>	84.5-85.5°	golden yellow	difficultly	74.5-75.5°	orange red	easily
Nitrovalerianicaldehydephenylhydrazone <sup>5</sup>	92.5-93°	“ “	“	51.5-52°	“ “	“
Benzoylformaldehydephenylhydrazone <sup>5</sup>	138°	yellow	“	114°	orange	“
“ <i>o</i> -nitro- “ <sup>5</sup>	141.5-142.5°	golden yellow	.....	113°	orange red	....
“ <i>m</i> - “ “ <sup>5</sup>	149-150°	orange brown	difficultly	139-140°	orange yellow	easily
Phenylhydrazonocyanacetic ester <sup>6</sup>	82°	.....	more	125°	.....	less
<i>m</i> -Nitro “ “ <sup>7</sup>	124-125°	light brown	difficultly	136-137°	yellow	easily
<i>p</i> - “ “ “ <sup>7</sup>	184°	yellow	“	168°	“	easily
<i>o</i> - “ “ “ <sup>7</sup>	146°	.....	“	116°	light yellow	“
α-Naphthylhydrazonocyanacetic ester <sup>8</sup>	147°	yellowish brown	.....	105°	brownish red	....

<sup>1</sup> Ber., 28, 340; 20, 613; 21, 428. <sup>2</sup> Ibid., 28, 2013. <sup>3</sup> Ann., 303, 16.

<sup>4</sup> Ber., 31, 1249. <sup>5</sup> Ibid., 34, 2001. <sup>6</sup> J. pr. Chem., 49, 321. <sup>7</sup> Ibid., 51, 219. <sup>8</sup> Ibid., 52, 160. A number of other derivatives of the hydrazone cyanacetic esters are described, but the colors of the α and β isomers are not given.

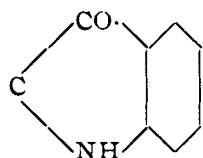
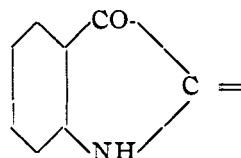
For diazocyanides, the *anti* forms are more deeply colored and have higher melting points.

The conclusions for the different classes of compounds are uncertain to

DIAZO COMPOUNDS.	Syn		Color	M.P.	Anti	
	M.P.				Color	Color
Benzenediazo-K-Sulphonate <sup>1</sup>	.....		intense orange	.....		light yellow
<i>o</i> -Chlor " " "	2	.....	intense red	.....		yellow
<i>p</i> -Chlor " " "	3	.....	light red	.....		"
<i>p</i> -Brom " " "	3	.....	"	.....		"
<i>m</i> -Brom " " "	3	.....	reddish orange	.....		"
2,4-Dibrom " " "	3	.....	.....	.....		"
2,4-Diod " " "	3	.....	light orange	.....		"
Potassium diazobenzene- <i>o</i> -sulphonate <sup>4</sup>			yellow	.....		light yellow
<i>p</i> -Toluenediazo-K-sulphonate <sup>5</sup>	.....		reddish yellow	.....		colorless
$\alpha$ -Naphthalenediazocyanide <sup>6</sup>	57-58°		.....	116°		reddish brown
$\beta$ - " " "	6	51-52°	yellow	131°		red
Anisol " " "	7	50-51°	orange red	121-122°		brownish red
<i>p</i> -Nitrodiazobenzene <sup>8</sup>	28-29°		yellowish brown	86°		fiery red
<i>p</i> -Chlor " " "	8	29°	yellow	105-106°		yellow or brown
<i>p</i> -Brom " " "	6	42°	yellow	129-130°		brown
<i>p</i> -Iod " " "	6	48°	yellowish brown	152°		reddish brown
<i>o</i> -Brom " " "	6	51°	yellow	107-108°		.....
2,4-Dibrom " " "	6	70-71°	yellow	141°		reddish brown
3,4- " " "	6	56-57°	yellow	100-101°		brown
2,5- " " "	6	42-43°	.....	122-123°		brick red
3,5- " " "	6	60°	yellowish red	85°		.....
2,6- " " "	6	44-45°	yellow	.....		.....
2,4,6-Tribrom " " "	6	59-60°	yellow	147°		brownish red
2,4,5- " " "	6	55°	yellow	100-101°		red

a greater or less extent, but the general conclusion is the point to which it is desired to draw attention. Since this is only a preliminary paper, the application of this principle to other compounds, such as the salts of nitrophenols, certain derivatives of succinylsuccinic ester and of dibenzalacetone, will not be made here<sup>9</sup>.

The structural formula of indigo is doubtless

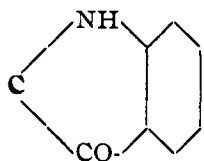
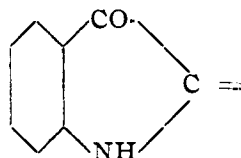


, the CO groups being in the *cis* position since it

<sup>1</sup> Ber., 27, 1726; <sup>2</sup> Ibid., 27, 3527; <sup>3</sup> Ibid., 27, 2530; 30, 75; <sup>4</sup> Ibid., 29, 1075; <sup>5</sup> Ibid., 30, 75; <sup>6</sup> Ibid., 30, 2529; <sup>7</sup> Ibid., 33, 2172; <sup>8</sup> Ibid., 28, 666.

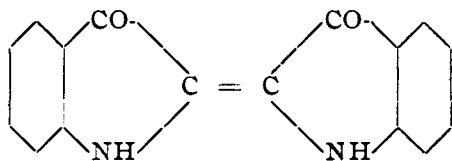
<sup>9</sup> Some weeks ago H. Ley (Z. angew. Chem., 31, 1308) called attention to these differences in color as dependent on configuration in some cases, but did not follow up the matter.

was only possible to obtain a monoxime<sup>1</sup>. There is the possibility of a stereoisomeric indigo which would be formulated

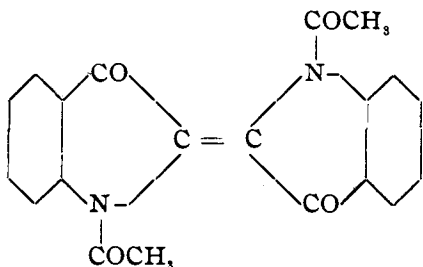


and which would be expected to possess a different

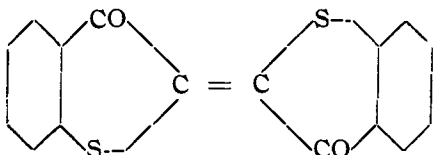
color from the ordinary indigo. Some time ago Lieberman and Dickhuth<sup>2</sup> described diacetyl indigo as being red in color. The replacement of hydrogen by an acetyl group does not in general cause such a marked change in color in colored organic compounds, so that the hypothesis may be put forward tentatively that there is a stereoisomeric change here, and that one geometrical isomer is colored blue and the other red. Some of the compounds containing the same chromophoric group as indigo are known and on the above hypothesis would be formulated:—



Indigo (blue)



Diacetylindigo (red)

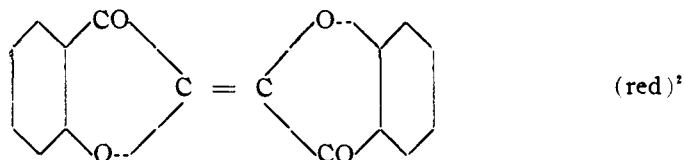
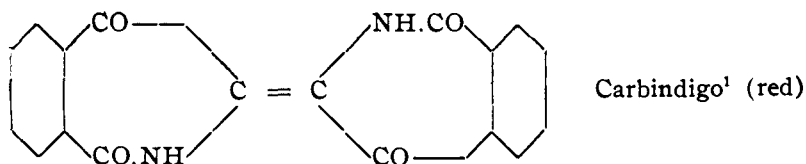


Thioindigo<sup>3</sup> (brownish red)

<sup>1</sup> Thiele and Pickard, Ber., 31, 1252.

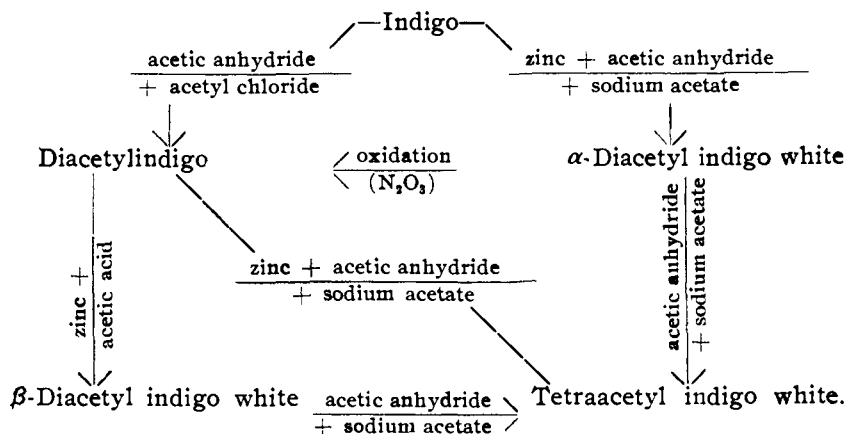
<sup>2</sup> Ber., 24, 4130.

<sup>3</sup> Friedländer, Ann., 351, 390.



Since no further work on diacetyl indigo was published, the subject was taken up at this point. Recently, however, Liebermann and Krauss<sup>3</sup> described some work on similar compounds so that the publication of this preliminary paper was decided upon although the two fields of work do not interfere.

The experimental work of Liebermann and Dickhuth was confirmed in all particulars and some of the relations cleared up. Since all the compounds have been described, only the general scheme of the manner of passing from one to another of these and the reagents best suited for the purpose will be given:—



Owing to their different solubilities in cold alkali Liebermann and Dickhuth ascribe to the two diacetyl indigo whites the groupings  $-\text{CO}-\text{CH}-\text{CH}-\text{CO}-$  for the  $\alpha$  and  $-\text{C}(\text{OH})=\text{C}=\text{C}(\text{OH})-$  for

<sup>1</sup> Gabriel and Colman, Ber., 33, 996.

<sup>2</sup> Friedländer and Neudörfer, Ber., 30, 1077; 32, 1837.

<sup>3</sup> Ber., 40, 2492.

the  $\beta$ . They state however that it is impossible to convert one directly into the other. A much more plausible explanation is that the  $\alpha$  being prepared from *cis* indigo directly is optically inactive diacetyl indigo white (by internal compensation—similar to mesotartaric acid), whereas the  $\beta$  is prepared from *trans* diacetyl indigo and is therefore a racemic mixture capable of being resolved into its optically active constituents.

The work on indigo is being continued.

LABORATORY OF ORGANIC CHEMISTRY,  
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### EXPERIMENTS UPON BARFOED'S ACID CUPRIC ACETATE SOLUTION AS A MEANS OF DISTINGUISHING GLUCOSE FROM MALTOSE, LACTOSE AND SUCROSE.

BY F. C. HINKEL AND H. C. SHERMAN.

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In some preliminary work upon the Barfoed test carried out in this laboratory by L. J. Cohen in 1905<sup>1</sup>, it appeared to be practicable to distinguish between glucose and maltose in solutions containing less than 0.02 per cent. of the former and at least as much as 0.2 per cent. of the latter, provided the tests are controlled by check experiments with known solutions of the sugars. These results seemed sufficiently favorable to warrant further experiment. The details of the test as used both in Cohen's experiments and in those described below are as follows:

*Reagent:* Dissolve 45 g. of neutral crystallized cupric acetate in 900 cc. of water, filter if necessary; add 1.2 cc. of 50 per cent. acetic acid and dilute to a liter. A portion of this reagent must show no change when heated in a boiling water-bath for 10 minutes, and on longer heating only a turbidity due to volatilization of acetic acid and formation of basic salt.

*Test:* To 5 cc. of the reagent in a test tube add the solution to be tested and stand the tube in a water-bath of such depth that the tube is surrounded by boiling water to at least the level of the liquid within. After  $3\frac{1}{2}$  minutes remove the tube from the water-bath and examine for cuprous oxide, viewing the tube against a black background in a good light. If no evidence of reduction is found, allow the tube to stand at room temperature for 5 or 10 minutes and examine again. For uniform results the different tubes used in making the tests should be of nearly the same diameter and thickness of wall. It is sometimes advantageous to pour out the liquid at the end of the test, leaving any cuprous oxide as far as possible adhering to the bottom of the test tube and examine again.

<sup>1</sup> Sherman's Methods of Organic Analysis, pp. 75-76.