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AROYLENEIMIDAZOLE DYES

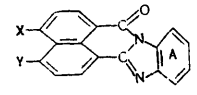
J. Arient

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I. INTRODUCTION

Aroyleneimidazole dyes are usually regarded as forming a separate group of synthetic dyes. They are characterised by the structure



The ring A may be substituted with various groups or fused rings, and positions X and Y may contain hydrogen atoms, various substituents, or another benzimidazole group[1-3].

For obvious reasons this group is also taken to include imides of *ortho*- or *peri*-dicarboxylic and tetracarboxylic acids, as well as compounds, obtained by the interaction of these acids with aromatic *peri*-diamines, which, although they contain no imidazole ring, are very similar to the parent compounds in method of preparation and dyeing properties.

The early aroyleneimidazole dyes were vat dyes. Their brilliance and beauty of shade, great fastness, and comparatively simple manufacture gave the impression that such dyes would displace thioindigoid dyes from the market.

The most important representative of the group of aroyleneimidazole dyes is Indanthren Scarlet GG (Vat

Scarlet 2J), which consists of a mixture of *cis*- and *trans*--naphthoylenebisimidazole — Indanthren Bordeaux RR (Vat Bordeaux) and Indanthren Brilliant Orange GR (Vat Brilliant Orange) — which are formed by the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine.

Development of the aroylenebenzimidazole dyes was halted for a long time, but during the past four or five years great interest has been renewed in dyes of this group, mainly based on naphthalene-1,8-dicarboxylic acid, which have found application as disperse dyes for the coloration of synthetic materials and fibres.

Besides the two main intermediates — naphthalene--1,4,5,8-tetracarboxylic and -1,8-dicarboxylic acids — other aromatic dicarboxylic acids have been used for the production of aroyleneimidazole dyes, e.g. naphthoylenebenzimidazole-*peri*-dicarboxylic acid, perylenetetracarboxylic acid, anthraquinone-2,3-dicarboxylic acid, pyrenic acid, etc.

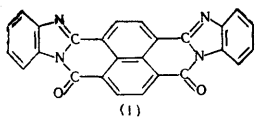
II. DYES BASED ON NAPHTHALENE-1,4,5,8-TETRACARBOXYLIC ACID

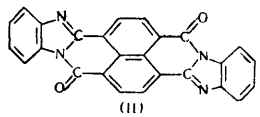
The practical use of *ortho*- and *peri*-diamines in the synthetic dye industry began during 1925–1930, when several patents appeared describing the interaction of *ortho*- and *peri*-diamines with naphthalene-1,4,5,8-tetracarboxylic acid. The insertion of a naphthalene ring system between two benzimidazole ring systems gave the necessary affinity of the dye for the fibre; the conjugated carbonyl groups facilitate the formation of leuco-compounds and their reoxidation.

The excellent dyeing properties of the dyes and the straightforward manufacturing process made possible the rapid development of the initial discoveries in this field.

1. Industrial Production of Indanthren Scarlet GG (Vat Scarlet 2J)

Indanthren Scarlet GG was the first and is still the most important of these dyes. It is formed by heating *o*-phenylenediamine with naphthalene-1,4,5,8-tetracarboxylic acid in glacial acetic acid[4-9]. The dye is not a pure substance: the reaction involves the formation of equal proportions of the *cis* (I) and *trans* (II) isomers.


(I)


(II)

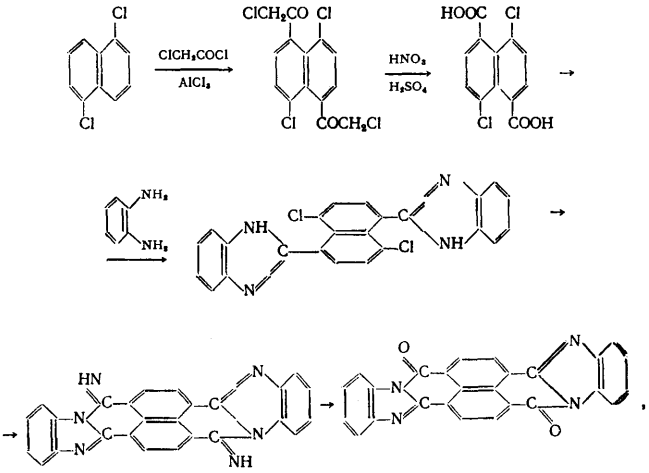
Both isomers can be isolated from the dye. Like all *trans* isomers of aroylenebenzimidazole dyes, (II) shows a hypsochromic shift in its absorption spectrum compared with the *cis* isomer.

The *trans* isomer appears on the market under the name Indanthren Brilliant Orange GR, and the *cis* isomer as Indanthren Bordeaux RR. Both are used as vat dyes for the dyeing of cotton. Whereas there is a great demand for the *trans* isomer because of its interesting shade, the Bordeaux finds limited use, and new applications are still being sought for it. The latter was placed on the market in a very finely divided form under the name Permanent Red TG Extra[10] as a colorant for lacquers, cellulose nitrate varnishes, and air-drying and stoving artificial--resin varnishes, and for the mass coloration of polymethacrylate, polystyrene, and polyethylene. It is distinguished by good fastness to solvents and to heat-treatment, and unusually high light fastness (grade 8 in cellulose nitrate varnish!). The orange dye is also suitable for similar application, and has been placed on the market as a pigment under the name PV Fast Orange GRL.[11]

The technical manufacture of Indanthren Scarlet GG itself is relatively straightforward. The process was originally conducted in boiling acetic acid[9]. The dye formed is accompanied by ~ 10% of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, which must be removed by subsequent treatment. It is more convenient to conduct the reaction in water containing 1–2% of sulphuric acid at a moderate pressure. Kinetic study of the process shows that the optimum temperature for the reaction is 120–130°. Decomposition products are formed at higher temperatures[12,13].

The dye is obtained in almost quantitative yield, without the formation of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, by working without a solvent at 140°, when both components are molten. The dye thus obtained contains rather more of the *trans* isomer, and hence has a more interesting shade than the dye synthesised as described above; its other dyeing properties are similar[14].

As already mentioned, the presence of both isomers in the final product is inconvenient for application. Methods were therefore sought for obtaining the pure *trans* isomer, or at least mixtures in which the content of the orange dye had been increased. A process was therefore worked out for preparing the pure orange dye by the scheme[15]



but this proposed synthesis cannot compete with the original method.

2. Effect of Solvent and Substituents on the Formation of Isomers of Indanthren Scarlet GG

The ratio of *cis* and *trans* isomers remains practically unchanged when a different solvent is used for the reaction, e.g. chlorobenzene, nitrobenzene, 2-ethoxyethanol,

glycerol, dimethylaniline. On the other hand, the relative proportions are changed fundamentally when halogen atoms are introduced into the positions 2,6 or 2,7 of the naphthalene-1,4,5,8-tetracarboxylic acid[16].

The above *trans* derivative is almost the sole product of the reaction of 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine, whereas the corresponding 2,7-dichloro-acid yields a monoaroylenebenzimidazole derivative. Measurement of the relative reaction velocities of 2,6- and 2,7-dichloronaphthalene-1,4,5,8--tetracarboxylic acids in comparison with the unsubstituted acid has established that at the same time the chlorine atoms slow down the reaction.

Analysis of the kinetic data and of the effect of steric, mesomeric, and inductive factors on the course of individual stages in the reaction indicates that the two consequences of the introduction of chlorine atoms into the molecule differ in origin. The general slowing down in the reaction is due to the fact that the chlorine atom impedes addition of the nitrogen atom of *o*-phenylenediamine by sterically blocking the neighbouring carbonyl carbon atom, while the effect on the relative proportions of *cis* and *trans* dye isomers is due to the fact that the chlorine atom, by mesomeric and inductive interaction, lowers the activity of the *ortho*-carbonyl group during final closing of the imidazole ring.

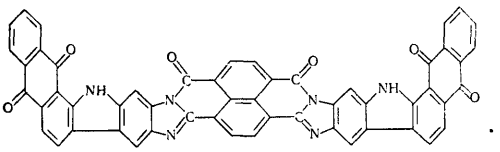
3. Oxidation of Naphthoylenebisbenzimidazole

According to the patent literature, oxidation of Indanthren Scarlet GG with sexivalent chromium in acid medium should yield Indanthren Brilliant Orange[17]. The product will be more or less yellowish or reddish depending on the quantity of oxidant employed; it is stated that oxidation of a mixture of the two isomers yields new dyes of quinoid character, whose shade moves towards the desired orange. However, oxidation of the pure *cis* isomer (Bordeaux) yields a dye similar in shade to the original dye[18]. The orange *trans* isomer also gives a dye similar in shade to the original dye. Oxidation of the individual isomers or of a mixture in 80% sulphuric acid, in which the dye dissolves completely (whereas in 60% sulphuric acid it is partly in suspension), yields dyes similar in shade to the original dyes.

Oscillographic polarography has proved that the structures of the *cis* and *trans* isomers remain unchanged on oxidation. These facts suggest that, during oxidation of a mixture of the isomers, neither undergoes chemical conversion to a dye of different shade; rather, the change in shade occurring during oxidation of the dye in suspension is due to the greater rate of reaction of the more soluble *cis* isomer compared with the less soluble *trans* isomer, with the formation of almost colourless products which are insoluble in alkalis.

4. Derivatives of Naphthoylenebenzimidazole

Chlorination of Indanthren Scarlet GG with chlorine in nitrobenzene[19] gives an orange vat dye, and chlorination with sulphuryl chloride gives a brown vat dye[20]. Bromination of Indanthren Bordeaux RR yields a dibromo-derivative, which on interaction with 1-aminoanthraquinone yields an anthrimide, cyclisation of which forms reddish--brown carbazole dyes[21].



When Indanthren Scarlet GG (or the individual isomers) is nitrated, orange and red pigments are obtained[22], which however, when applied as vat dyes, give greys and blacks on cotton[19] owing to reduction of the nitro-groups during vatting.

By using the corresponding substituted *ortho*-diamines, we can obtain various substituted aroylbenzimidazole dyes of various shades. Of the large number of dyes obtained in this way, Indanthren Printing Brown B, synthesised by the interaction of 4-ethoxyphenylene-1,2-diamine and naphthalene-1,4,5,8-tetracarboxylic acid, and Indanthren Printing Brown 5R, obtained by reaction of 4-chlorophenylene-1,2-diamine with the same acid, have found industrial application[4,7].

Dyes prepared by the use of *ortho*-diamines of the naphthalene[19], phenanthrene[23], and fluorene[24] series have not found application because of solubility difficulties during vatting.

On the other hand, dyes for which 1,2- and 2,3-diaminoanthraquinones are used as the amine component appear to be very interesting. When such diamines react with naphthalene-1,4,5,8-tetracarboxylic acid in high-boiling solvents, vat dyes are formed which produce on cotton olive shades of high fastness properties[25].

Some of the *ortho*-diamines which are not very readily available can be replaced in the reaction by the corresponding *ortho*-nitroamino-[26] or *ortho*-aminoazo-compounds[27]. The intermediates formed when they react with naphthalene-1,4,5,8-tetracarboxylic acid are further reduced in alkaline medium with sodium sulphide or dithionite, or else with iron in acid medium with simultaneous formation of the naphthoylenebenzimidazole skeleton.

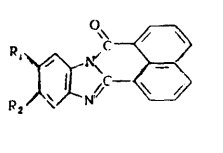
III. SEPARATION OF ISOMERIC AROYLENEBENZIMIDAZOLES

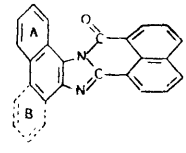
As already mentioned in the previous Section, reaction of *ortho*- or *peri*-dicarboxylic or tetracarboxylic acids with aromatic *ortho*- or *peri*-diamines involves the formation of mixtures of isomers of the corresponding aroylenebenzimidazoles. Various technical processes are available for the separation of these isomers, and can in principle be divided into four groups. (*a*) The mixture of isomers is dissolved at an elevated temperature in an alkali-metal alkoxide or amide; on cooling, the insoluble *trans* derivative separates, while the soluble *cis* derivative is obtained by acidifying the filtrates[28]. (*b*) A solution of the dye in concentrated sulphuric acid (or chlorosulphuric acid) is cautiously diluted with water; at first the less soluble sulphate of the *trans* isomer separates, and after its removal the *cis* isomer is obtained by further dilution[29]. (*c*) The technical dye is stirred into mixtures of organic sulphonic acids and organic solvents, and separation is effected by use of the differing solubilities of salts of the individual isomers[30]. (*d*) The mixture is stirred into chlorosulphuric acid in the presence of hydrochloric, hydrobromic, or sulphuric acid, and the insoluble *trans* form is filtered off[31].

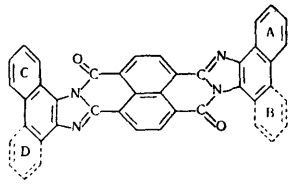
All these processes are directed primarily towards obtaining the pure, coloristically more valuable *trans* isomer from the dye produced by the interaction of naphthalene-1,4,5,8-tetracarboxylic acid and *o*-phenylenediamine. The *cis* isomer contains almost all the impurities formed in this reaction, which comprise firstly those soluble in alkalis and organic solvents (mainly naphthoylenebenzimidazole-*peri*-dicarboxylic acid) and secondly impurities which are soluble solely in organic solvents.

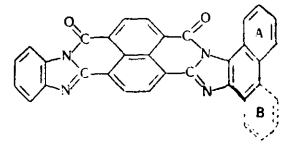
The steadily increasing demand for Indanthren Bordeaux RR as a pigment is responsible for the more exacting purity requirements. The very pure *cis* and *trans* isomers are obtained by a somewhat modified process[32], in which the sparingly soluble adduct of the *trans* isomer with potassium ethoxide is separated in a medium containing excess alcohol, while the *cis* isomer is isolated from the filtrate by alkaline hydrolysis after salting-out in water[32].

Only two isomers are formed in the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine. The number of isomers increases when substituted *ortho*-diamines are used. It has not proved possible to separate these isomers by a technical process. Only partial separation, i.e. into *cis* and *trans* isomers, is achieved. Several aroyleneimidazole dyes can be separated into their isomers by chromatography[33]. Dyes (I)–(VI) have been separated chromatographically on aluminium oxide, and the fluorescence spectra of the resulting isomers determined.



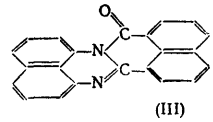




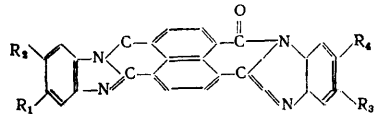


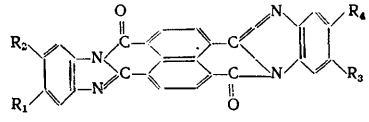
(Ia) $R_1 = OC_2H_5$; $R_2 = H$,
(Ib) $R_1 = H$; $R_2 = OC_2H_5$,

(IIa) Benzene ring in position A,
(IIb) Benzene ring in position B,



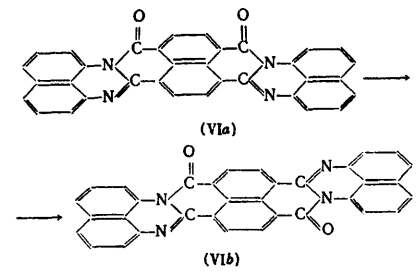
(III)





(IVa) $R_1, R_2 = OC_2H_5$; $R_3, R_4 = H$,
(IVb) $R_1, R_4 = OC_2H_5$; $R_2, R_3 = H$,
(IVc) $R_3, R_4 = OC_2H_5$; $R_1, R_2 = H$,
(Va) Benzene rings in positions A and C,
(Vb) Benzene rings in positions B and C,
(Vc) Benzene rings in positions B and D,

(IVd) $R_1, R_2 = OC_2H_5$; $R_3, R_4 = H$,
(IVe) $R_1, R_4 = OC_2H_5$; $R_2, R_3 = H$,
(Vd) Benzene ring in position A,
(Ve) Benzene ring in position B.



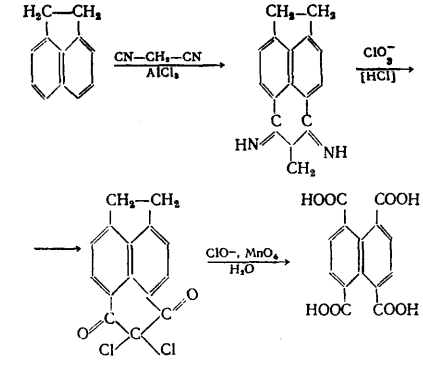
(VIa)

(VIb)

IV. PRODUCTION OF NAPHTHALENE-1,4,5,8-TETRACARBOXYLIC ACID

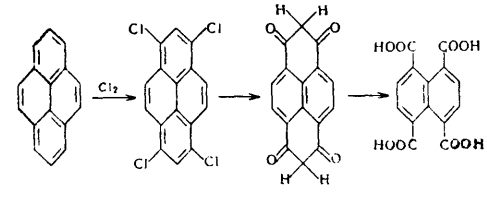
The principal intermediate in the manufacture of aroyleneimidazole dyes, naphthalene-1,4,5,8-tetracarboxylic acid, is obtained mainly in two ways.

The first process[34-36] starts from acenaphthene and is conducted according to the scheme



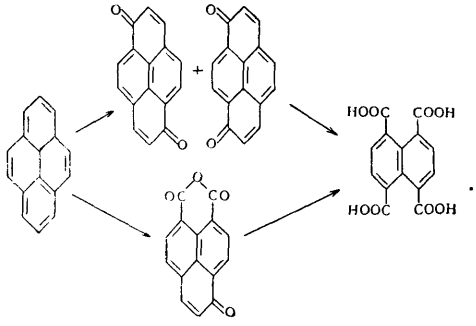
The second process starts from pyrene, from which naphthalene-1,4,5,8-tetracarboxylic acid can be obtained by chlorination or oxidation.

When chlorination is used, the chlorination or bromination of pyrene is followed by oxidation of the tetrahalogenopyrene:



According to the literature[37-40] high yields are obtained by this method, but technologically it makes increased demands on the equipment. A simpler process is oxidation, which, furthermore, does not require complicated

apparatus. The course of the process can be clearly represented by the following scheme



The oxidation of pyrene to a mixture of pyrene-3,8- and -3,10-quinones and pyrenic acid has been known since 1870.[41] The structure and properties of these substances have been investigated by several workers[42-51]. Pyrenequinones and pyrenic acid are obtained by oxidising pyrene with chromic mixture in aqueous suspension or with chromium trioxide in acetic-acid solution. Subsequently pyrenequinones were also obtained by the oxidation of pyrene with hydrogen peroxide in glacial acetic acid[52]. This last method is unsuitable for the manufacture of pyrenequinones, since it requires the use of a large excess of a comparatively expensive oxidant, and the oxidation product is insufficiently pure.

The oxidation of pyrene with chromium trioxide in acetic acid was mentioned in the very early literature, but a more detailed method has been given only in a patent[53] of the Rütgerswerke AG. In this method double the theoretical quantity of chromium trioxide is used, and the reaction mixture is boiled; a quantitative yield of almost 100% quinone is formed. However, the industrial application of this method is impeded by the high cost of acetic acid.

The oxidation of pyrene in suspension with chromic mixture has been examined in greatest detail by Bamberger and Philip[44-46] and in the patent mentioned above[53]. According to Bamberger, finely ground pyrene is oxidised by the theoretical quantity of dichromate in sulphuric acid diluted with five volumes of water. The paper gives neither the precise temperature conditions nor the yield and purity of the product, only that the latter contains pyrenic acid. Bamberger's results were checked by Vollmann[39], who does not give the procedure but describes in greater detail the reaction product, allegedly obtained in 90% yield; it contained hardly any unchanged pyrene and only a few per cent of pyrenic acid. The Rütgerswerke patent contains quite contradictory data on the substance obtained by Bamberger and Philip's method, and states that the reaction product consists of 36% of pyrenequinones, 14% of chromic salts, 50% of unchanged pyrene, and traces of pyrenic acid. The patent gives a recipe according to which 98–99% quinones can be obtained in almost quantitative yield. This recipe differs from Bamberger and Philip's procedure in the quantity of dichromate used (178% of theoretical) and a smaller quantity of sulphuric acid. Here, too, the temperature conditions of the reaction are given in insufficient detail.

It follows from the contradictions in the literature quoted that insufficient study has been made of the conditions for the oxidation of pyrene to pyrenequinones, and that the oxidation process is very sensitive to variation in the conditions.

The oxidation of pyrene to pyrenequinones with hydrogen peroxide in acetic acid and with oxygen or air in the presence of a catalyst has been described. Owing to the unsatisfactory course of the oxidation, neither method is applicable to manufacture.

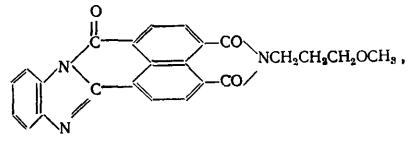
Naphthalene-1,4,5,8-tetracarboxylic acid can be obtained from the pyrenequinones (or pyrenic acid) by oxidation in either acid or alkaline medium. In acid medium excess of oxidant (dichromate in dilute sulphuric acid) is used. Pyrenic acid, which itself was obtained in low yield, is supposedly converted into naphthalenetetracarboxylic acid in quantitative yield. The yield of the latter acid from pyrenequinones is insignificant. This method of oxidation forms the subject of a 1932 patent of the IG. Farbenindustrie AG.[54], according to which pyrene is dissolved in concentrated sulphuric acid and, after dilution with water, oxidised with excess of dichromate. The intermediate oxidation products, pyrenequinones, are not isolated. The yield of naphthalenetetracarboxylic acid is not high.

Considerably better results are achieved by oxidising pyrenequinones in alkaline medium. Information on this method is given only in two patents dating from 1933. According to the first patent[55] pyrenequinones or pyrenic acid are oxidised in alkaline medium by heating with excess of permanganate solution; the excess of permanganate remaining should accelerate crystallisation of the naphthalenetetracarboxylic acid from solution after acidification, and is removed in the purification of the acid. According to published data, the yield of naphthalenetetracarboxylic acid by this method is 70–75% based on the pyrene taken for the reaction. The second patent[56] describes the use of an alkaline solution of sodium hypochlorite or of a mixture of bleaching powder and calcium hydroxide for the oxidation. The operating technique is very simple: a suspension of pyrenequinones is stirred up with an alkaline solution of sodium hypochlorite, and the mixture allowed to stand for a few hours at room temperature and then for a few hours at 50–80°. The quinones are converted into naphthalenetetracarboxylic acid, which is isolated. According to the patent the yield is 70–80% based on the pyrenequinones.

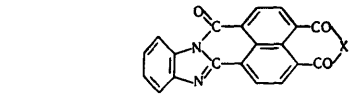
V. DYES BASED ON NAPHTHOYLENEBENZIMIDAZOLE-*peri*-DICARBOXYLIC ACID

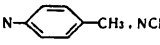
Besides the symmetrical dyes obtained by reaction of naphthalenetetracarboxylic acid with two moles of an *ortho*-diamine, unsymmetrical dyes can also be synthesised. When the acid reacts with *o*-phenylenediamine in aqueous medium in the presence of sodium acetate, equimolar cyclisation yields the so-called naphthoylenebenzimidazole-*peri*-dicarboxylic acid[57-59], which can react further with other variously substituted aromatic *ortho*- or *peri*-diamines or else with aliphatic or aromatic amines. In the former case, vat dyes of various shades are formed[62], and in the latter case disperse dyes[63].

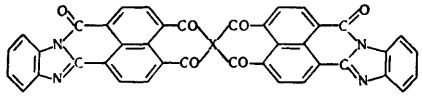
Among disperse dyes of this type, Samaron Brilliant Yellow HRL[60] having the structure[61]

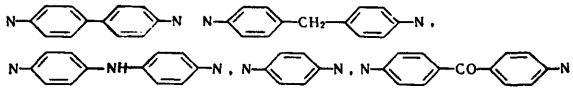


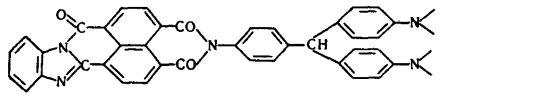
has appeared on the market. This group includes also dyes of types (I)–(V)

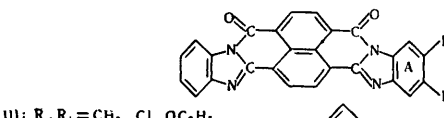


I: X = O, NH, NCH_3, , NCH_2CH_2OH, , NCH_2CH_2CN, $N(CH_2)_7CH_3$, $N(CH_3)_{17}CH_3$

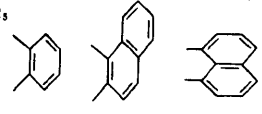


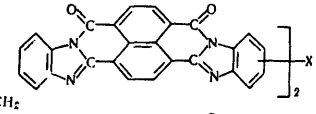
II: X = 

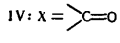


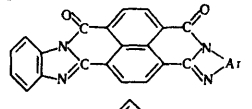


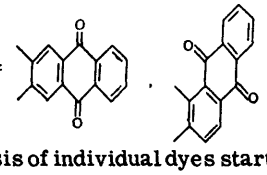
III: R, R_1 = CH_3, Cl, OC_2H_5

A = 

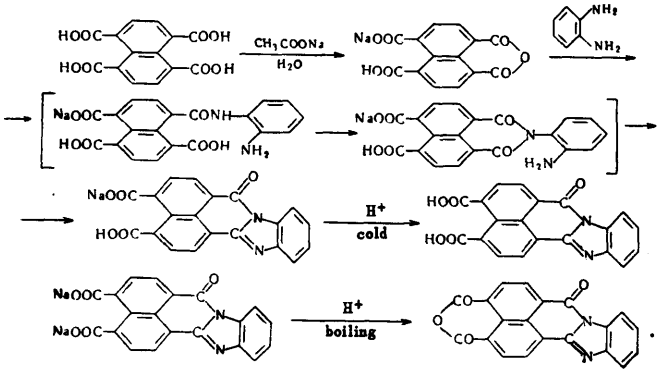


IV: X = 

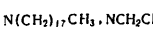


V: Ar = 

The synthesis of individual dyes starts from naphthoylenebenzimidazole-*peri*-dicarboxylic acid (X), which is made to react with various aliphatic or aromatic amines. This acid is obtained, according to patent information[59], by the reaction of naphthalene-1,4,5,8-tetracarboxylic acid with one molecule of *o*-phenylenediamine in aqueous sodium acetate solution. The disagreement on the mechanism of this reaction encountered in the literature has been cleared up by Arient and Dvořák, who suggest the following scheme to explain the course of the reaction[64]



These workers have established the relation between the structure and the spectra of dyes of types (I)–(V).[64] The effect of substituents in dyes of this type on the bathochromic shift in the absorption band increases in the sequence

O, NCH_3, $N(CH_2)_{17}CH_3$, NCH_2CH_2OH, , , NH, NCH_2CH_2CN.

These dyes can be employed as either vat or disperse dyes. With lengthening of the aliphatic chain, dyeing power is lost owing to the insolubility of the vat; dyeing power also decreases as the chain becomes longer when the compounds are used as disperse dyes.

The doubling of the naphthoylenebenzimidazole-*peri*-dicarboxylic acid moiety in dyes of type (II) results in a bathochromic shift in colour compared with dyes of type (I). The element uniting the two moieties of the dye molecule has hardly any perceptible effect. The dyes can be applied as vat dyes with good fastness properties.

The absorption spectrum of dyes of type (III) is considerably affected by substituents — methyl, chlorine, and ethoxyl — in the molecules of symmetrical and unsymmetrical aroylenebenzimidazoles. In contrast to the previous types (I) and (II), these dyes exhibit a considerable bathochromic shift, and they yield reds, violets, and browns. The influence of substituents is strongly marked within this group; their bathochromic effect increases in the sequence H, CH_3, Cl, $2CH_3$, OC_2H_5. Dyes formed from naphthoyleneimidazole-*peri*-dicarboxylic acid with naphthylene-1,2- and -1,8-diamines exhibit a further shift in the absorption band towards longer wavelengths. Analogous results have been obtained for naphthalene-1,4,5,8-tetracarboxylic acid.

All dyes were separated into *cis* and *trans* isomers, which showed an analogous variation in colour to that observed with their mixtures. Most of the dyes, mainly derivatives of naphthoylenebenzimidazole-*peri*-dicarboxylic acid, are distinguished by their brilliance and excellent fastness, and can be used as vat dyes. Dyes derived from naphthalenetetracarboxylic acid are sparingly soluble (with the exception of naphthoylenebisbenzimidazole), so that they cannot be used as vat dyes. Dyes containing the naphthalene ring system have inadequate fastness.

The influence of naphthoylenebenzimidazole-*peri*-dicarboxylic acid on the relative proportions of *cis* and *trans* isomers formed in the synthesis of such dyes was checked, its reaction with *o*-phenylenediamine being taken as example. The ratio of these isomers obtained with such a consecutive synthesis was practically 1 : 1, equal to the ratio obtained by the direct interaction of naphthalene-1,4,5,8-tetracarboxylic acid with *o*-phenylenediamine. This indicates that naphthoylenebenzimidazole-*peri*-dicarboxylic acid exerts no influence on the formation of one isomer or the other.

Dyes of type (IV), i.e. dyes having two naphthoylenebisbenzimidazole moieties, have been obtained by the reaction of naphthoylenebenzimidazole-*peri*-dicarboxylic acid with 3,3′,4,4′-tetraaminobenzophenone and with diphenylmethane-3,3′,4,4′-tetraamine. In the former case the dye contains one double conjugated system, but in the latter case it contains two conjugated systems isolated from one another by the methylene bridge. A dye resulting from the diphenylmethanetetra-amine has a red colour with a moderate hypsochromic shift in comparison with naphthoylenebisbenzimidazole; a dye from the tetraaminobenzophenone shows practically the same absorption.

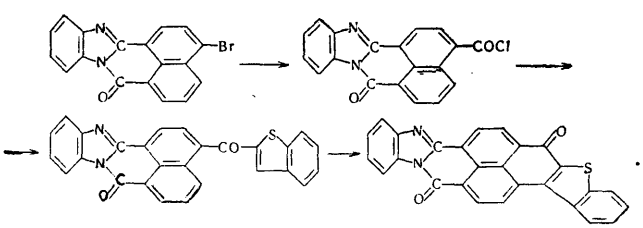
Dyes of type (V), which result from the reaction of naphthoylenebenzimidazole-*peri*-dicarboxylic acid with 1,2- and 2,3-diaminoanthraquinone, exhibit a large bathochromic shift towards reddish browns and browns.

VI. DYES BASED ON NAPHTHALIC (NAPHTHALENE--1,8-DICARBOXYLIC) ACID

Interest in this group of dyes has arisen during the past four or five years. They are suitable for use as disperse dyes for the coloration of polyester, polyamide, polyvinyl, and polyethylene fibres. They are distinguished by brilliance, thermal stability, and excellent fastness to light, organic solvents, gas fumes, and sublimation.

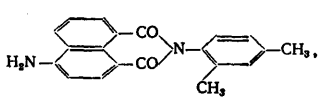
1. Preparation of Dyes

These dyes are obtained by the reaction of naphthalic acid with various substituted aromatic diamines (yellows and oranges with intense fluorescence) or *peri*-diamines (reds and violets) in an organic solvent. Derivatives of 1,2-*peri*-naphthoylenebenzimidazole are the most interesting. Many of its derivatives, with chlorine, bromine, alkyl, alkoxyl, hydroxyl, nitro, acylamino, etc. substituents, have been described in the patent literature [65-69]. Derivatives of this intermediate are also used, according to the patent literature, as intermediates for the synthesis of brown vat dyes [70].

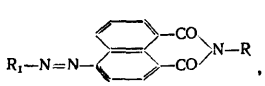


The process for obtaining naphthaloperinone dyes, which are formed by the reaction of naphthalic acid with naphthylene-1,8-diamine, is analogous to the preparation of naphthoylenebenzimidazole dyes [71-75]. A whole range of derivatives having various substituents has been patented [76-78]. Orange and red lakes for the mass coloration of polyamides and polyesters can be obtained by the sulphonation of some substituted naphthaloperinones, the resulting sulphonic acids being precipitated as their barium salts [79].

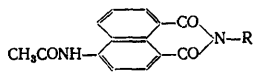
Naphthalimides are employed to a less extent as disperse dyes. They are obtained by the action of ammonia or primary amines on naphthalic anhydride. Among such dyes are Celliton Brilliant Yellow FF2



for cellulose acetate rayon, red and brown disperse dyes of the type [80]



and fluorescent brightening agents of the type [81,82]

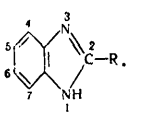


where R = H, Alk, Ar and R_1 = Ar.

The introduction of substituents into the dye produces a change in their shade. Nitration occurs especially readily; the resulting mono- or di-nitro-derivatives can be used firstly as individual dyes and secondly as intermediates for the synthesis of new compounds.

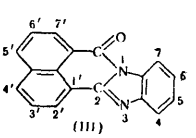
2. Substituted 1,2-*peri*-Naphthoylenebenzimidazoles

The work of Efros on the nitration of simple 2-alkyl and 2-aryl derivatives of benzimidazole showed that the presence of the imidazole ring in the benzimidazole molecule disturbs the distribution of electrons in the benzene ring, in the sense that the 5–6 bond approaches a single bond in character, while the 4–5 and 6–7 bonds become more nearly double bonds. This explains the unusual course of several substitutions, for example the dinitration of 2-methylbenzimidazole, when 2-methyl-5,6-dinitrobenzimidazole is formed [84].



Arient and Marhan [85] subjected 1,2-*peri*-naphthoylenebenzimidazole (III) and its 3'-, 4-, 4'-, 5-, 6-, and 7-nitro-derivatives to nitration. Each isomer was nitrated under identical conditions, by the action of the nitrating mixture on a solution of the original compound in concentrated sulphuric acid at 20°. The products were isolated by salting-out the solution into water. The course of the nitration was investigated chromatographically. The mono- and di-nitro-compounds formed were identified by comparing their electronic spectra with those of known specimens.

The nitration of 1,2-*peri*-naphthoylenebenzimidazole yields a single compound, which was identified as the 6-nitro-derivative. In the nitration of 4'-nitro-1,2-naphthoylenebenzimidazole, too, a nitro-group enters position 6, with the formation of 4',6-dinitro-1,2-*peri*-naphthoylenebenzimidazole, and the nitration of 3'(and 6')-nitro-1,2--*peri*-naphthoylenebenzimidazole yields 6,3'(and 6')--dinitro-1,2-*peri*-naphthoylenebenzimidazole



(III)

The high reactivity of position 6 is due to the activating effect of the non-acylated nitrogen in position 3, reaction at the *ortho* position in the benzene ring (position 4) evidently being sterically hindered. The activating influence of the lone electron pair on the other, acylated nitrogen in position 1 is distributed between the acylating part of the molecule and the benzene ring (in lesser degree). This result is fully consistent with mathematical calculation of

the electron distribution at individual carbon atoms in the naphthoylenebenzimidazole structure[86], according to which the reactivity of the carbon atoms diminishes in the sequence 6, 5, 6′, 3′.

Further nitration of derivatives of 1,2-*peri*-naphthoylenebenzimidazole in which the nitro-group is located in positions 4–7 in the benzene ring involves entry of the second nitro-group in position 6′. A nitro-group in position 5 or 7 prevents entry of the next nitro-group in position 6, which is the most active. A nitro-group in position 4 deactivates the benzene ring, and interferes with the activating influence of the lone electron pair of the non-acylated nitrogen.

In the synthesis of known derivatives of 1,2-*peri*-naphthoylenebenzimidazole, these workers have also investigated, apart from methods of preparation, the influence of substituents in *o*-phenylenediamine or in naphthalic acid on the course of the reaction[87].

Reaction of naphthalic anhydride with 4-nitrophenylene-1,2-diamine may yield 5- and 6-nitro-1,2-*peri*-naphthoylenebenzimidazole (IX) and (IV). The effect of the nitro-group on the basic character of the two amino-groups in nitro-*o*-phenylenediamine has not yet been accurately established, but the influence of the nitro-group in nitroanilines on the variation in pH is well known. The course of the reaction can be approximately predicted on the basis of these results. The weakening of electron density on the amino-nitrogen *para* to the nitro-group induces great reactivity in the second amino-group, and consequently preferential formation of *N*-(2-amino-5-nitrophenyl) naphthalimide (II: R = NO_2), which is converted with ring-closure into 6-nitro-1,2-*peri*-naphthoylenebenzimidazole (IV). In fact, the reaction of naphthalic anhydride with 4-nitrophenylene-1,2-diamine has been used to synthesise the 6-nitro-derivative (IV) as the main product, whereas the 5-nitro-isomer (IX) was formed in far smaller quantity; the latter was identical with a substance obtained from 2,4-dinitroaniline and naphthaloyl dichloride (XVI). Their interaction gave *N*-(2,4-dinitrophenyl)naphthalimide (XIV: R = NO_2), which was partly reduced, the resulting *N*-(2-amino-4-nitrophenyl)naphthalimide (VIII: R = NO_2) then being converted into the pure 5-nitro-isomer (IX). The yield of 6-nitro-1,2-*peri*-naphthoylenebenzimidazole from 2,5-dinitroaniline and naphthaloyl dichloride is not very high. The *N*-(2,5-dinitrophenyl)naphthalimide (XV: R = NO_2) formed in this reaction is hydrolysed to a considerable extent on reduction. The reactivity of 2,4-dinitroaniline is so low that it reacts only with the dichloride (XVI). A similar conclusion was reached by Krasovitskii and Matskevich, who obtained negative results for the reaction of naphthalic anhydride with nitroanilines[83].

The 4- and 7-nitro-1,2-*peri*-naphthoylenebenzimidazoles were obtained in an analogous manner. Reaction of 3-nitrophenylene-1,2-diamine with naphthalic anhydride gives only one of the two possible isomers, to which Arient and Marhan ascribe the structure 4-nitro-1,2-*peri*-naphthoylenebenzimidazole (XIX). The isomeric 7-nitro-derivative (XVIII) is formed by reaction of the dichloride (XVI) with 2,6-dinitroaniline. Owing to considerable steric hindrance, reaction takes place with great difficulty and gives a low yield.

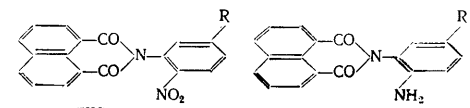
Naphthoylenebenzimidazole derivatives containing substituents in the naphthalene ring or in both the naphthalene and the benzene rings have been obtained by methods similar to that employed to obtain the benzene-substituted derivatives[85]. Reaction of 3-nitrophthalic acid with *o*-phenylenediamine and its mononitro-derivatives gave 3′(and 6′)-nitro- and 4,3′(and 6′)- and 6,3′(and 6′)-dinitro--1,2-*peri*-naphthoylenebenzimidazoles; 4-nitrophthalic acid similarly gave the 4′(and 5′)-nitro- and the 4,4′(and 5′)- and 6,4′(and 5′)-dinitro-derivatives.

An *ortho*-diamine containing a chlorine atom behaves in a more specific fashion than a nitro-derivative. Reaction of 4-chlorophenylene-1,2-diamine with naphthalic anhydride (I) begins at the amino-group *para* to the chlorine atom, the final product being 5-chloro-1,2-*peri*-naphthoylenebenzimidazole (X), which is identical with the compound prepared from 4-chloro-2-nitroaniline and naphthaloyl dichloride (XVI) by a method analogous to the synthesis of 5-nitro-1,2-*peri*-naphthoylenebenzimidazole. For comparison, 6-chloro-1,2-*peri*-naphthoylenebenzimidazole (V) was obtained also by Sandmeyer's reaction from the amine resulting from the reduction of the 6-nitro-derivative (IV).

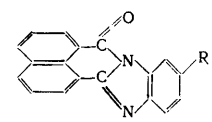
Naphthalic anhydride (I) was then made to react with 4-methylphenylene-1,2-diamine and 3,4-diaminobenzoic acid. In both cases reaction occurred with that amino--group which had become the more reactive under the influence of the remaining substituent. As was to be expected, 4-methylphenylene-1,2-diamine yielded mainly 5-methyl-1,2-*peri*-naphthoylenebenzimidazole (XI), together with a smaller quantity of the 6-methyl isomer. The isomers could not be separated chromatographically, but the acids obtained by their oxidation were separated chromatographically and identified. 1,2-*peri*-Naphthoylenebenzimidazole-5-carboxylic acid was obtained by oxidising pure 5-methyl-1,2-*peri*-naphthoylenebenzimidazole, prepared by fusing 4-methyl-2-nitroaniline with the anhydride (I). With permanganate or dichromate in sulphuric acid hardly any oxidation occurs (only traces of the corresponding acids were obtained).

Almost quantitative oxidation was accomplished by the action of oxygen in glacial acetic acid in the presence of a cobalt compound as catalyst.

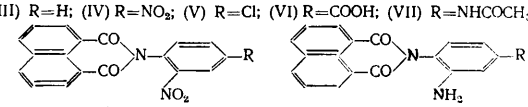
The final product of reaction of the anhydride (I) with 3,4-diaminobenzoic acid was 1,2-*peri*-naphthoylenebenzimidazole-6-carboxylic acid (VI).



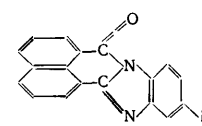
(XV) (II)



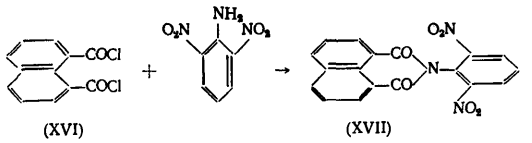
(III) R=H; (IV) R=NO_2; (V) R=Cl; (VI) R=COOH; (VII) R=$NHCOCH_3$



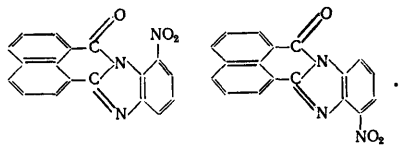
(XIV) (VIII)



(X) R=NO_2; (X) R=Cl; (XI) R=CH_3; (XII) R=COOH; (XIII) R=$NHCOCH_3$



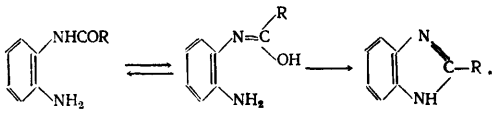
(XVI) (XVII)



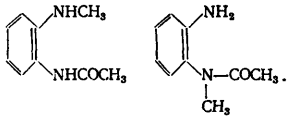
(XVIII) (XIX)

3. Interaction of Benzene-1,2,4,5-tetraamine with Dicarboxylic Acids

Many workers have investigated the reaction of aromatic *ortho*-diamines with carboxylic acids. Benzimidazoles were first obtained by this method by Phillips[88], by interaction of the components in boiling dilute hydrochloric acid. High yields were obtained with aliphatic acids, whereas aromatic acids reacted very feebly. Roeder and Day[89] explained the formation of benzimidazole compounds by a mechanism involving an intermediate monoacyl derivative



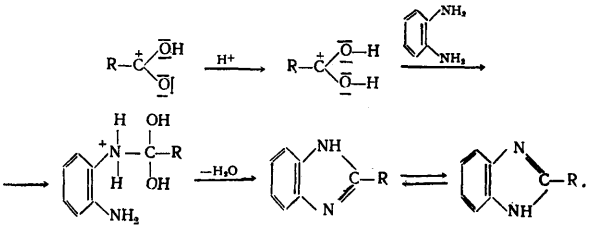
At the same time it was established that the postulated intermediate compound should be capable of enolisation, since the compound (II), unlike (I), is incapable of forming an imidazole ring.



(I) (II)

The synthesis of imidazole derivatives by Phillips' method has been widely investigated and developed by Soviet workers, who have established[90] that the concentration of hydrochloric acid used greatly affects the yield. The reaction was conducted by heating equimolecular quantities of the *ortho*-diamine with the carboxylic acid in dilute hydrochloric acid medium in sealed tubes at 150–180°. By this method 2-aryl derivatives were also obtained in high yields. With increase in the hydrochloric acid concentration the yield of the benzimidazoles first increased to a definite level, after which the yield fell again.

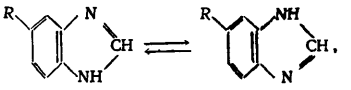
The optimum hydrochloric acid concentration differs for different carboxylic acids and also diamines. Hydrochloric acid forms salts with the amine, and this retards the reaction, since the amine reacts as the free base. The main factors determining the yield obtained are the concentration of the hydrochloric acid and the basic strength of the amine: it was concluded from the results[91,92] that hydrochloric acid of lower concentration must be used with amines which are stronger bases. However, the highest yield was achieved with *o*-phenylenediamine: other *ortho*-diamines, which were stronger or weaker bases, gave lower yields. The effect of the hydrochloric acid on the carboxylic acid is to diminish the ionisation of the latter, and the addition of a proton to the polarised oxygen atom of the carboxyl results in a positive charge on its carbon atom. From measurements of the dissociation constants of the acids, Porai-Koshits and Kharkharova drew the significant conclusion that reactivity decreases in the sequence — aralkane-, alkane-, and arene-carboxylic acid — and that the optimum concentration of hydrochloric acid should be higher the higher the degree of dissociation of the carboxylic acid. On the basis of these results a new mechanism was then proposed for the formation of benzimidazole derivatives



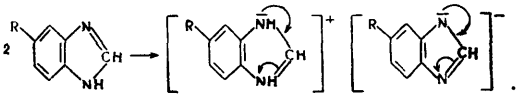
It has recently been established[93] that polyphosphoric acid could be used to obtain high yields of alkyl and aryl derivatives of benzimidazole.

Efros investigated substitution reactions in benzimidazole and its derivatives[94-97], and found that no clear substitution rules exist for the benzene ring in benzimidazole, although positions 5 and 6 are more active than the others. The nitration of benzimidazole, for example, yields only the 5,6-dinitro-derivative. His results demonstrated that, under the influence of the imidazole ring, the benzene ring loses its aromatic character, in the sense that the bond between the rings and the 4–5 and 6–7 carbon–carbon bonds approach double bonds in character.

The unsuccessful earlier attempts to isolate the two hypothetical isomers



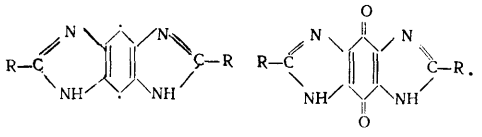
are explained by the ease of their tautomeric interconversion[98]. Study of the amphoteric character of benzimidazole proved significant for an understanding of some of its properties[99]. In acid medium it exists as a cation, whereas in alkaline medium its acid properties are developed, and the corresponding anion is formed. Among salts of benzimidazole, the greatest interest attaches to those which can be used for the gravimetric determination of certain metals. In neutral medium benzimidazole can exist in a state of equilibrium between the hypothetical cationic and anionic forms



Efros prepared[94] several derivatives of linear diimidazobenzene (III) by reducing 5,6-dinitrobenzimidazole, and

then treating the resulting *ortho*-diamine with a carboxylic acid. Whereas the first imidazole ring is formed readily under mild conditions, it was necessary to work under pressure to close the second ring. Both symmetrical and unsymmetrical derivatives can be obtained in this way. Earlier Kym and Ratner[100] had synthesised 2,6-dimethyldiimidazobenzene (V) by fusing 5,6-diaminobenzimidazole with anhydrous sodium acetate and acetic anhydride. This derivative was described also by Ruggli and Fischer[101], who synthesised it by the action of acetic anhydride on the substance obtained by reducing supposedly pure 4,6-diphenylazophenylene-1,3-diamine. The properties of substances described by different workers differ somewhat.

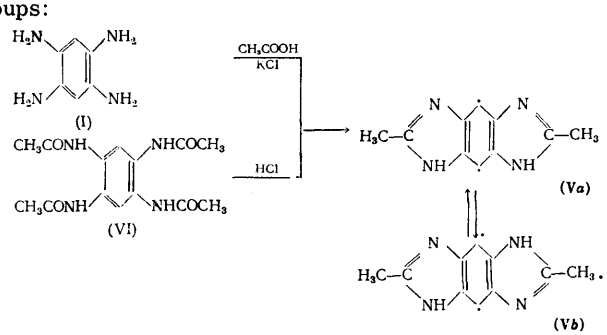
The above effect of the imidazole ring on the benzene ring in benzimidazole stabilises the double bond between the rings. This entails an increase in electronic charge at the free *meso* positions in the linear diimidazobenzene (III), which appears in their considerable radical unsaturation[102,103]. In their properties these compounds show a notable resemblance to anthracene, especially in their ease of oxidation to the quinones (IV).



(III) (IV)

Arient and Marhan have established[104] that the direction of the reaction depends on the medium in which it occurs. Prolonged boiling of the tetraamine with 90% acetic acid gives the linear 2,6-dimethyldiimidazobenzene (V). Heating the tetraamine (I) with acetic anhydride yields 1,2,4,5-tetraacetamidobenzene (VI) in addition to (V). In the presence of an equivalent quantity of anhydrous sodium acetate to neutralise the hydrogen chloride present in the tetrahydrochloride of the tetraamine, only (VI) is formed. Substitution in the imidazole ring obviously requires the presence of dissociated hydrochloric acid, which catalyses the reaction. In dilute acetic acid, where hydrochloric acid is liberated on hydrolysis of the benzene-1,2,4,5-tetraamine hydrochloride, only the diimidazo-derivative is formed.

In anhydrous medium, formation of the latter, which occurs to a considerably smaller extent, is accompanied by acetylation of the amino-groups of the tetraamine. In the presence of a substance which will combine with hydrogen chloride, ring-closure is completely suppressed, the sole process being acetylation of all the amino-groups. The resulting 1,2,4,5-tetraacetamidobenzene (VI) is stable in aqueous medium, and is not hydrolysed on being heated; boiling in hydrochloric acid readily converts it into the diimidazo-derivative with the elimination of two acetyl groups:



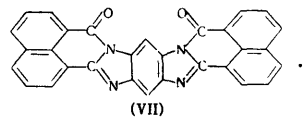
The two workers obtained the highest yield of (V) by treating the tetraamine with acetic acid in dilute hydrochloric acid medium under pressure at 180°. Their results agree well with those obtained by Porai-Koshits and his coworkers[90,91] in the synthesis of 2-alkylbenzimidazoles. In this case, too, the yield of benzimidazole first increased with increase in the concentration of hydrochloric acid, reached a definite maximum, and fell again.

Reaction in water and 5–20% hydrochloric acid gives the diimidazobenzene (V) as the main product. In more concentrated hydrochloric acid the hydrolysis of the benzenetetraamine hydrochloride, which itself cannot react, is in considerable measure suppressed, and a large part of it remains unchanged at the end of the reaction. Use of excess of acetic acid slightly increases the yield. The fine white crystalline needles of the compound (V) obtained are completely homogeneous, and their properties do not indicate the existence of two isomers (V*a*) and (V*b*). By analogy with benzimidazole it can be assumed that these represent two tautomeric forms of the same substance. The compound (V) is also amphoteric in character, dissolving in dilute acids and forming salts (mostly insoluble in the cold) with several metals.

The tetraamine reacts with formic, phenylacetic, and cinnamic acids under the same conditions as with acetic acid. With formic acid, the linear diimidazobenzene (III: R = H), similar in properties to the dimethyl derivative (V), is formed. Similarly, phenylacetic acid yields the 2,6-dibenzyldiimidazobenzene (III: R = $C_6H_5CH_2$), and 5-amino-2-benzyl-6-hydroxybenzimidazole as by a product. When cinnamic acid is used, the 2,6-distyryldiimidazobenzene (III: R = $C_6H_5CH:CH$), which possesses an intense fluorescence, is formed.

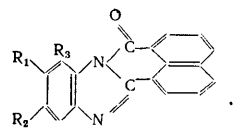
Benzoic acid and benzoyl chloride do not react with benzenetetraamine; nor does the more reactive *p*-nitrobenzoic acid give the expected compound, but decomposes under the reaction conditions. The behaviour of these acids had been investigated earlier[105].

On the basis of a study of the simpler linear diimidazobenzenes, Arient and Marhan attempted to obtain the bisaroyleneimidazo-derivative (VII) by reaction of the tetraamine with naphthalic acid[106].



(VII)

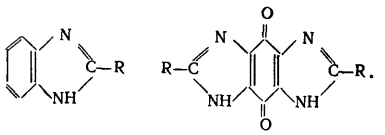
Instead of the suggested compound (VII), however, the principal reaction product was 5,6-diacetamido-1,2-*peri*-naphthoylenebenzimidazole (VIII). Doubt is cast on data given in a French patent[107], describing the preparation of a diimidazo-derivative, since a monoimidazole is also formed when the reaction is carried out under severe conditions — in boiling tetrahydronaphthalene — as indicated in the patent.



(VIII) $R_1 = R_3 = CH_3CONH$; $R_2 = H$; (IX) $R_1 = CH_3CONH$; $R = R_3 = H$; (X) $R_1 = CH_3COO$; $R_2 = R_3 = H$; (XI) $R_1 = R_2 = CH_3CONH$; $R_3 = CH_3$.

The main product contains, besides unchanged naphthalic acid, also 5-acetamido-1,2-*peri*-naphthoylenebenzimid-azole (IX) and 5-acetoxy-1,2-*peri*-napthoylenebenzimid-azole(X).

The formation of only one ring can be explained by distortion of the electron cloud of the benzene ring in the tetraamine resulting from the action of the aroyleneimidazole ring. A series of detailed investigations was made[108-111] on the effect of the imidazole ring on the electron distribution of the benzene ring in benzimidazole derivatives (XII). The results show that the benzene ring loses its aromatic character, and the bond between the rings approaches closely to a double bond in character. The simplest compounds of the diimidazo-type resemble anthracene in their chemical properties, mainly in their ease of oxidation to quinones (XIII).



(XII) (XIII)

In conformity with this work, it may be supposed that the loss of symmetry and hence of aromatic character in the benzene ring of compound (VIII), resulting from the effect of the aroyleneimidazole structure, is so great that the 4–5 and 6–7 carbon–carbon bonds approach double bonds in character, while the 5–6 bond becomes more nearly a single bond. Consequently the carbon atoms at positions 5 and 6 appear as the two ends of the conjugated system of benzimidazole, which are subject to the action of the heterocyclic nitrogen atoms. This breakdown in the uniform distribution of the electron cloud of the benzene ring has an unfavourable effect on the formation of the diimidazo-compound.

The benzenetetraamine can be replaced in the synthesis of 5,6-diacetamido-1,2-*peri*-naphthoylenebenzimidazole (VIII) by 4,6-dinitrophenylene-1,3-diamine. This reacts in an analogous manner with naphthalic acid in glacial acetic acid medium on simultaneous reduction of the nitro-groups with iron. Application of the same method to 3,5-diphenylazotoluene-2,6-diamine gave the dye (XI), whose properties were analogous to those of the benzene derivative.

4. Mechanism of Interaction of Phthalic Anhydride with *o*-Phenylenediamine

Products of the condensation of *o*-phenylenediamine with phthalic anhydride were described in the earlier papers, the results being well known[112,113]. Depending on the stoichiometric proportions of the components and the reaction conditions, *o*-phthalimidoaniline (II), *o*-benzimidazol-2′-ylbenzoic acid (III), 1,2-*o*-benzoylenebenzimidazole (IV), *o*-bisbenzimidazol-2′-ylbenzene (V), and *o*-diphthalimidobenzene (VI) were obtained. By the reaction of phthaloyl dichloride with *o*-phenylenediamine, Stetter prepared[114] a compound having an eight-membered ring (VII). Porai-Koshits and Antoshul'skaya[115] investigated the production of compounds (III)–(VI) by fusing the components in various proportions, and found that the diphthaloyl derivative (VI) is formed with the greatest difficulty, whereas compounds (III) and (V), which contain imidazole rings, are more readily formed. The compound (IV), unlike other aroyleneimidazole compounds, exhibits properties characteristic of lactam rings, and can be cleaved to give *o*-benzimidazol-2′-ylbenzoic acid and its derivatives.

In order to explain the interrelationship of the individual stages in the conversion, Arient and Marhan examined the reaction of *o*-phenylenediamine with phthalic anhydride under mild conditions[116]. They found that two amino-compounds are formed initially, one existing for a very short time and being present in very small amount. This is probably the addition product (I). When the boiling point is reached, only the amino-compound (II) is present in the mixture, and the imidazole derivative (III) is formed. The composition of the mixture remains almost unchanged on further heating, the reaction product containing the two compounds in roughly equal proportions.

The reaction in methanol is considerably affected by the presence of hydrochloric acid. As its concentration increases, the quantity of the imidazole derivative (III) first increases at the expense of the amino-compound (II), and at the same time *o*-bisbenzimidazol-2′-ylbenzene (V) is also formed; when 0.5 equivalent of hydrochloric acid is used per mole of *o*-phenylenediamine, (V) becomes the main reaction product.

Further increase in the concentration of hydrochloric acid leads again to the formation of the amino-compound (II) as the final reaction product. The highest yield is obtained in the presence of one equivalent of hydrogen chloride; the amine hydrochloride which is formed crystallises out, and reaction ceases. The hydrochloric acid concentration is so decisive that variation in the relative proportions of the starting materials has no effect on the course of the reaction.

Reaction of *o*-phenylenediamine with phthalic anhydride at higher temperatures yields mainly *o*-benzimidazol-2′-ylbenzoic acid (III). In the presence of one equivalent of hydrochloric acid in water, the amino-compound (II) and traces of the imidazole derivative (III) are at once formed on heating, whereas in methanol the sole reaction product is the amino-compound (II). On further heating, the amount of the compound (III) increases, the proportions of the two compounds being 1 : 1 after 1 h and only compound (III) remaining after 2–3 h.

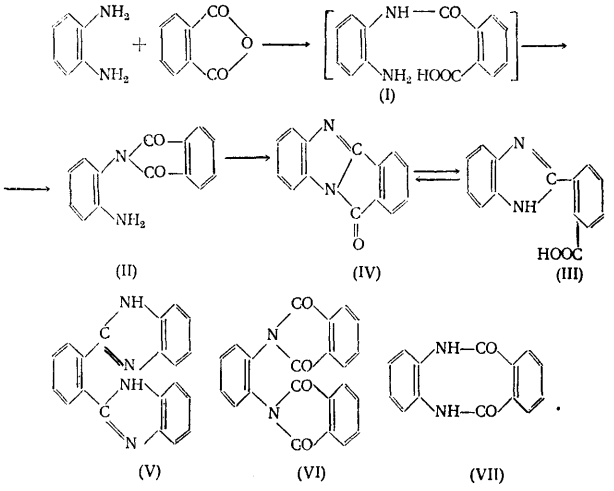
In the presence of hydrochloric acid under pressure at 180°, the reaction gives no typical maximum yield[90,91] at an optimum hydrochloric acid concentration, in contrast to the preparation of benzimidazole derivatives from *o*-phenylenediamine and monocarboxylic acids. The reaction in water is anomalous, with the formation of *o*-diphthalimidobenzene (VI).

In acetic acid reaction follows the same course as in water. As soon as the boiling point is reached, the initially formed amino-derivative (II) passes quantitatively into the imidazole (III) together with a small amount of 1,2-*o*-benzoylenebenzimidazole (IV) and the bisimidazole derivative (V). Reaction products of the same composition are formed in pyridine. The use of nitrobenzene accelerates the reaction and increases the quantity of 1,2-*o*-benzoylenebenzimidazole (IV) in the final product.

1,2-*o*-Benzoylenebenzimidazole (IV) is obtained from (II) and (III) by fusion at 250–290° or boiling in acetic anhydride. In contrast to 1,2-*peri*-naphthoylenebenzimidazole, which is readily formed when *o*-phenylenediamine and naphthalic acid are heated in acetic acid, the reaction of *o*-phenylenediamine with phthalic anhydride terminates under these conditions with the formation of the imidazole (III), the compound (IV) being present in the mixture in very small amount. Closure of the second five-membered ring requires great deformation of the molecule, which can be achieved under severe conditions.

Examination of the rearrangement of *o*-phthalimidoaniline (II) to *o*-benzimidazol-2′-ylbenzoic acid (III) revealed that the hydrochloride of the amino-compound remains unchanged even after heating in methanol for several hours, and the same result is obtained after adding various quantities of either hydrochloric acid or sodium carbonate. In water rearrangement occurs quantitatively after 2–3 h, and hydrochloric acid has no effect on the course of the reaction. High-boiling organic solvents (pyridine, acetic acid, nitrobenzene) accelerate the rearrangement, but the reaction product also contains 1,2-*o*-benzoylenebenzimidazole. Rearrangement leading to the formation of the imidazole derivative is, of course, facilitated by raising the temperature, and probably involves an intermediate stage of formation of 1,2-*o*-benzoylenebenzimidazole (IV), which in aqueous medium, however, is almost immediately hydrolysed to *o*-benzimidazol-2′-ylbenzoic acid (III).

If the process takes place in anhydrous medium (in acetic anhydride or on fusion), reaction stops at the first stage. In high-boiling solvents, partial hydrolysis by water formed in the reaction occurs. On the basis of the above results, the following mechanism has been suggested for the reaction.



5. Mechanism of Interaction of Naphthalic Acid with *o*-Phenylenediamine

Products of the interaction of naphthalic acid with *o*-phenylenediamine do not possess properties analogous to those of the benzene derivatives. These compounds have been described in less detail, and probably not always entirely correctly. Bistrzycki and Risi[118] obtained from *o*-phenylenediamine and naphthalic anhydride the amide (I), which on being heated to 230–240° was converted into 1,2-*peri*-naphthoylenebenzimidazole (m.p. 189°). Both compounds were later obtained by the same method by Chakravarti[119], who also described 8-benzimidazol-2′-ylnaphthoic acid (V). The 1,2-*peri*-naphthoylenebenzimidazole prepared in a similar manner[120,121] melted at 206°. Krasovitskii and Matskevich[122] obtained negative results for the reaction of naphthalic acid with *o*-nitroaniline, but by simultaneous reduction they isolated[123] *N*-*o*-aminophenylnaphthalimide (II) together with 1,2-*peri*-naphthoylenebenzimidazole (m.p. 189°). It is interesting that papers on the hydrolytic cleavage of benzimidazole derivatives make no mention of the possibility of the cleavage of naphthoylenebenzimidazole, although the analogous benzoylenebenzimidazoles are extremely labile to hydrolysis.

In a study of the interaction of *o*-phenylenediamine with naphthalic acid, Arient and Marhan established that the temperature of the medium has a decisive influence on the direction of the reaction[124]. At temperatures up to 60° in various solvents, the amide (I) is gradually formed, and from it *N*-*o*-aminophenylnaphthalimide (II). In all cases the final reaction product is the imide (II), containing a minute amount of 1,2-*peri*-naphthoylenebenzimidazole (IV).

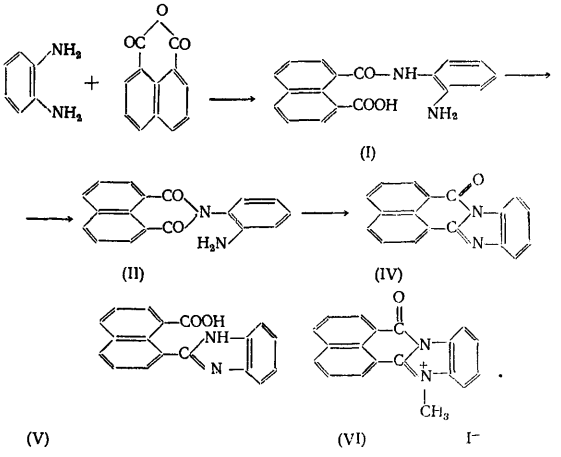
The undoubted formation of the amino-compound (II) is not consistent with results obtained for the reaction of *o*-phenylenediamine with phthalic anhydride. In the latter case not only amino-compounds of types (I) and (II) but also *o*-benzimidazol-2′-ylbenzoic acid and *o*-bisbenzimidazol-2′-ylbenzene are formed under analogous conditions. The proportions of these products are decisively affected by the content of hydrochloric acid in the reaction mixture.

When naphthalic acid is used, analogous benzimidazole derivatives are not formed with the most varied changes in reaction medium.

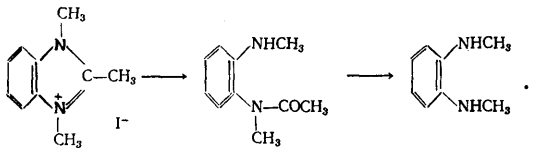
Interaction at higher temperatures leads to the formation of 1,2-*peri*-naphthoylenebenzimidazole. Reaction occurs very readily, especially in boiling acetic acid, and with a quantitative yield, as well as when *N*-*o*-aminophenylnaphthalimide or the starting materials are heated. The course of the reaction is not affected by additions of various quantities of hydrochloric acid, which is the effective agent in the synthesis of benzimidazole derivatives.

The 1,2-*peri*-naphthoylenebenzimidazole obtained is very stable, and does not undergo cleavage on prolonged boiling or heating at higher temperatures under pressure, either in acid or in alkaline medium. This distinguishes it significantly from the analogous 1,2-*o*-benzoylenebenzimidazole, which is so readily hydrolysed that the final reaction product from *o*-phenylenediamine and phthalic anhydride is *o*-benzimidazol-2′-ylbenzoic acid. An absolutely anhydrous medium is required for the preparation of 1,2-*o*-benzoylenebenzimidazole. The great stability of 1,2-*peri*-naphthoylene-1′,2′-benzimidazole means that the reaction of *o*-phenylenediamine with naphthalic acid does not proceed beyond the stage at which it is formed, and the postulated imidazole derivative (V) cannot be obtained.

The following reaction mechanism has been suggested on the basis of the above results



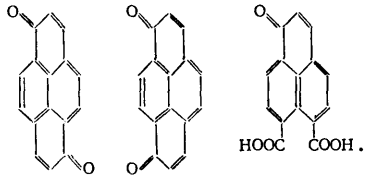
Several methods have been developed for cleaving the imidazole ring in benzimidazole derivatives, among which the most convenient is in most cases alkaline hydrolysis of the 1,2,3-trialkyl derivatives[125-127]



1,2-*peri*-Naphthoylenebenzimidazole forms with methyl iodide a methiodide (VI). Even in this case, however, the naphthoylenebenzimidazole derivative behaves differently from simple benzimidazoles. This compound (VI) is as stable as the original 1,2-*peri*-naphthoylenebenzimidazole, and is not cleaved by any of the usual methods.

VII. DYES BASED ON PYRENIC ACID

The oxidation of pyrene yields naphthalene-1,4,5,8--tetracarboxylic acid, a necessary intermediate for the synthesis of several vat dyes. A mixture of pyrene-1,6- and -1,8-quinones (I) and (II) can be isolated as intermediate oxidation products, together with 1-oxophenalene--6,7-dicarboxylic acid (III), which is termed pyrenic acid in the literature.



(I) (II) (III)

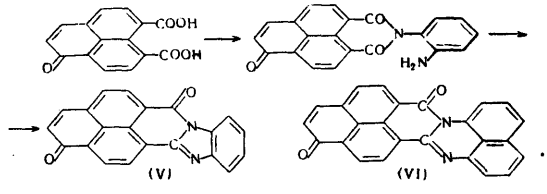
Pyrenic acid was first obtained by Hintz[128], and isolated in pure form by Goldschmiedt[129], its structure later being determined by Bamberger and Philip[46]. More recently its preparation has been mentioned in a paper by Vollmann et al.[130] The only method available for preparing pyrenic acid is that given by Bamberger and Philip, who oxidised pyrene in aqueous suspension with a slight excess of chromic mixture (6 instead of 5.3 moles calculated as chromium trioxide). Oxidation is not complete. Pyrenic acid was isolated from the reaction products by extraction with dilute sodium carbonate solution at 50°. The residue remaining after extraction was again subjected to further oxidation. Complete oxidation of the pyrene was achieved after six repetitions of the oxidation process. The yield of the unpurified acid is 20.6%. Our results indicate that, apart from resinous impurities, this acid still contains ~20% of naphthalene-1,4,5,8-tetracarboxylic acid. The pyrenic acid is purified by several recrystallisations from acetic acid. The yield of the pure acid was not indicated in the early work[46]. Its anhydride, obtained by prolonged heating above 100°, does not melt, but chars at 260°. Vollmann gives for it m.p. 174°. In a more detailed study of the oxidation of pyrene to pyrenic acid in aqueous suspension, Arient and Dvořák established that the low yield of the acid is due to the fact that a large proportion of the pyrene is oxidised to compounds which dissolve readily in water, or to carbon dioxide.

A method was developed for the identification of naphthalene-1,4,5,8-tetracarboxylic acid which consisted in treating it with *o*-phenylenediamine to form a scarlet aroyleneimidazole dye. Pyrenic acid, which gives a yellow spot on a chromatogram, is converted into a brownish-orange dye by reaction with *o*-phenylenediamine.

Bromination of pyrenic acid in acetic acid yields a monobromo-derivative. Neither increasing the excess of bromine nor prolonging the duration of reaction produces further bromination. The bromine is probably present in position 2 in pyrenic acid, by analogy with the bromination of pyrenequinone, in which the bromine enters positions 2 and 7, and also from the fact that oxidation of the brominated pyrenic acid with alkaline hypochlorite solution yields naphthalene-1,4,5,8-tetracarboxylic acid containing no bromine.

Reaction of pyrenic acid or its bromo-derivative with *ortho*- or *peri*-diamines of the benzene or naphthalene series in glacial acetic acid gives an almost theoretical yield of aroyleneimidazole (V) or naphthaloperinone (VI) dyes[117].

A mixture of *cis* and *trans* isomers can theoretically be formed by the reaction. However, the compounds obtained could not be separated into two isomers either by the usual methods or chromatographically. The dyeing properties also indicate that the dyes are single compounds. It may be suggested that, under the influence of the keto--group in the nucleus of pyrenic acid, the electron density will decrease on the carbonyl carbon nearer to the keto--group, which after initial formation of the corresponding imide will take part preferentially in formation of the imidazole ring:



(V) (VI)

Unlike the products obtained from naphthalic acid, these substances are vatted with *ortho*- or *peri*-diamines. Some of the dyes of this type and their characteristic properties are listed in the accompanying Table.

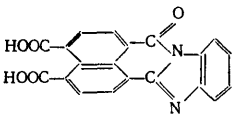
Bromination of the dye obtained from pyrenic acid and *o*-phenylenediamine yields monobromo- and dibromo--derivatives. The first bromine atom enters the ring containing the keto-group, probably at position 4. The monobromo-derivative is identical with the product of the interaction of 4-bromopyrenic acid and *o*-phenylenediamine. Oxidation of the monobromo-derivative with hypochlorite or with alkaline potassium permanganate solution gives naphthoylenebenzimidazole-*peri*-dicarboxylic acid, which contains no halogen.

The second bromine atom enters the benzene ring of the imidazole. Oxidation with hypochlorite yields naphthoylenebenzimidazole-*peri*-dicarboxylic acid (VII) containing one bromine atom in the molecule. More severe oxidation with chromium trioxide in acetic acid forms a tetracarboxylic acid containing no bromine, to which the structure (VIII) has been assigned on the basis of the work of Bamberger and Berlé[131] and of Efros and his coworkers,

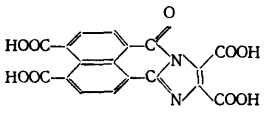
TABLE.

Acid	Diamine	Colour of dye	Colour of vat	Shade
Pyrenic	o-phenylene-diamine	yellowish brown	orange with green fluorescence	brownish orange
»	4-chlorophenyl-ene-1,2--diamine	ditto	ditto	reddish brown
»	4-ethoxyphenyl-ene-1,2--diamine	reddish brown	»	pure brown
»	naphthylene--1,2-diamine	dark brown	orange	violet-brown
»	naphthylene--1,8-diamine	blue-black	red	khaki
Monobromo-pyrenic	o-phenylene-diamine	brownish orange	orange with green fluorescence	orange-brown

and which forms with *o*-phenylenediamine orange-coloured reaction products.



(VII)



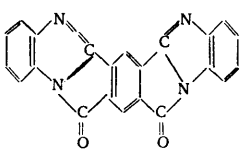
(VIII)

The aroylenebenzimidazole or aroyleneperinone dyes obtained give interesting and brilliant shades on cotton from a vat, but these are less fast to washing than shades obtained with available vat dyes.

VIII. DYES BASED ON BENZENE-1,2,4,5-TETRACARBOXYLIC ACID

Benzene-1,2,4,5-tetracarboxylic acid has attracted the attention of chemists because of the possibility of obtaining dyes analogous to those of the aroyleneimidazole series from naphthalene-1,4,5,8-tetracarboxylic acid. Little work has been done on the reactions of pyromellitic acid, apart from the formation of functional derivatives. The preparation of complex compounds with thiourea has been described[132], and also the use of pyromellitic anhydride with 2-methylquinoline for the synthesis of benzoindanones[133].

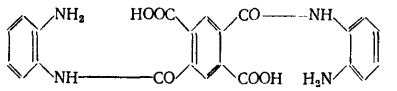
The only mention of the reaction of this acid with aromatic diamines is contained in a Swiss paper of 1941, which describes also 1,2,4,5-benzoylene-1′1′,1″,2″-dibenzimidazole[134]. The paper describes the preparation of the *trans* isomer of terephthaloylenebisbenzimidazole (I) by fusing pyromellitic anhydride with the appropriate quantity of *o*-phenylenediamine. The structure of this compound was postulated without further explanation, and was supported by elementary analysis.



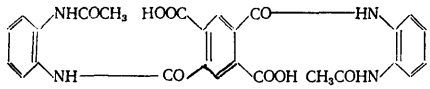
(I)

Formation of the *trans* isomer would be of great interest for the dye industry, since by using various substituted *o*-phenylenediamines it would be possible to obtain a range of dyes which could be vatted and would be of interest as disperse dyes.

Arient and Havlíčková have obtained the compounds (II) and (III) together with a mixture of other products by the reaction of *o*-phenylenediamine with pyromellitic acid in acetic acid[135].

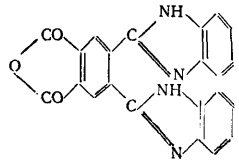


(II)



(III)

Reaction of *o*-phenylenediamine with pyromellitoyl tetrachloride in chlorobenzene gave a mixture of two compounds, which were separated by means of their solubility difference. One of them could be vatted in ammoniacal medium, from which it colours cotton an orange shade; this is the *trans* isomer of terephthaloylenebisbenzimidazole (I). The second substance could not be vatted, melts above 400°, and has the structure (IV).



(IV)

IX. DYES BASED ON PHTHALIC ACID

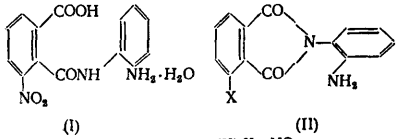
The mechanism of the interaction of *o*-phenylenediamine with monocarboxylic and *ortho*- or *peri*-dicarboxylic acids presupposes the initial addition of the lone pair of electrons on the amino-nitrogen to the carbonium ion formed by protonation of the carboxy-group. According to this mechanism a carboxy-group having a diminished electron density on the carbon atom will react preferentially. The magnitude of the electron density on the carboxy-carbon will depend on the nature and position of substituents in the aromatic ring of the carboxylic acid. Krasovitskii et al.[136] point to the formation of a single isomer of naphthoylenebenzimidazole when 4-nitronaphthalic acid reacts with *o*-phenylenediamine. On the above considerations this isomer was assumed to be 1,2-(4-nitronaphth-1,8-oylene)benzimidazole. A similar conclusion was drawn by Arient and Marhan when discussing the results of the reaction of various nitronaphthoic acids with *o*-phenylenediamine and of nitro-*o*-phenylenediamine with naphthalenedicarboxylic acid[87,116].

Nitro- and acetamido-groups present in phthalic anhydride should exert different effects on the formation of nitro- and acetamido-benzoylenebenzimidazoles respectively: 3-nitrophthalic anhydride should yield 1,2-(6′-nitrobenz-1′,2′-oylene)benzimidazole (VII), and 4-nitrophthalic

anhydride the corresponding 4'-nitro-derivative (XIII) or the corresponding intermediate products. The acetamido--group should have the opposite effect: 3-acetamidophthalic anhydride should give 1,2-(3'-acetamidobenz--1',2'-oylene)benzimidazole (XXIII), and 4-acetamidophthalic anhydride the corresponding 5'-acetamido--derivative (XXV).[152]

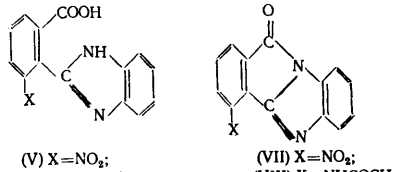
Paper chromatography indicates that four compounds are formed by the reaction of 3-nitrophthalic anhydride with *o*-phenylenediamine. Among them have been identified 2-benzimidazol-2'-yl-3-nitrobenzoic acid (V), 1,2-bisbenzimidazol-2'-yl-3-nitrobenzene (IX), and the hydrate of 2-*o*-aminophenylcarbamoyl-3-nitrobenzoic acid (I). The fourth compound could be neither isolated nor identified. The corresponding 1,2-(6'-nitrobenz-1',2'--oylene)benzimidazole (VII) was obtained by subliming the benzimidazolylbenzoic acid (V) or boiling it in acetic anhydride.

Reduction of (V) and (IX) followed by acetylation of the resulting amino-derivatives effected the synthesis of 3-acetamido-2-benzimidazol-2'-ylbenzoic acid (VI) — together with 1,2-(6'-acetamidobenz-1',2'-oylene)benzimidazole (VIII) — and 3-acetamido-1,2-bisbenzimidazol--2'-ylbenzene (X).



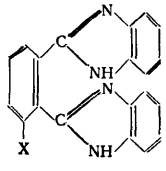
(I) (II)

(II) X=NO_2;
(III) X=NH_2;
(IV) X=$NHCOCH_3$



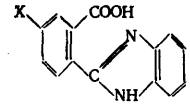
(V) X=NO_2;
(VI) X=$NHCOCH_3$;

(VII) X=NO_2;
(VIII) X=$NHCOCH_3$.

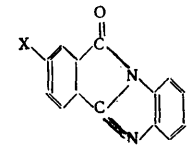


(IX) X=NO_2;
(X) X=$NHCOCH_3$.

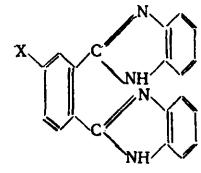
All three compounds formed by the reaction of 4-nitrophthalic anhydride with *o*-phenylenediamine — 2-benzimidazol-2'-yl-5-nitrobenzoic acid (XI), 1,2-bisbenzimidazol-2'-yl-4-nitrobenzene (XVI), and 2-*o*-aminophenylcarbamoyl-5-nitrobenzoic acid (XIX) — have been identified. 1,2-(4'-Nitrobenz-1',2'-oylene)benzimidazole (XIII) is formed only when the benzimidazole (XI) is sublimed or is boiled in acetic anhydride; it was not detected among the initial reaction products. Reduction of the diimidazole (XVI) followed by acetylation gave 4-acetamido-1,2-bisbenzimidazol-2'-ylbenzene (XVIII); reduction of the benzimidazole (XI) gave the amino-derivative (XII), which on being boiled in acetic acid was converted into 1,2-(4'-acetamidobenz-1',2'-oylene)benzimidazole (XV). The same substance was obtained also by the acetylation of (XIV), synthesised from the amino-acid (XII) by sublimation.



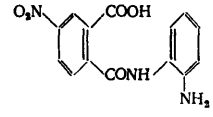
(XI) X=NO_2;
(XII) X=NH_2;



(XIII) X=NO_2;
(XIV) X=NH_2;
(XV) X=$NHCOCH_3$.



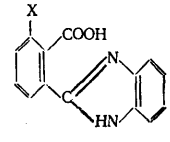
(XVI) X=NO_2;
(XVII) X=NH_2;
(XVIII) X=$NHCOCH_3$.



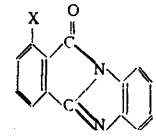
(XIX)

Reaction of 3-acetamidophthalic anhydride with *o*-phenylenediamine yields seven compounds — 1,2-(3'-aminobenz--1',2'-oylene)benzimidazole (XXII) and its *N*-acetyl derivative (XXIII), 2-amino-6-benzimidazol-2'-ylbenzoic acid (XX) and its *N*-acetyl derivative (XXI), 3-acetamido--1,2-bisbenzimidazol-2'-ylbenzene (X), 3-amino-*N*-*o*--aminophenylphthalimide (III), and 3-acetamido-*N*-*o*--aminophenylphthalimide (IV).

Hydrolysis of the acetyl group is observed not only on reaction in dilute hydrochloric acid under pressure but also under milder conditions, even in methanol.

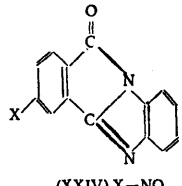


(XX) X=NH_2;
(XXI) X=$NHCOCH_3$

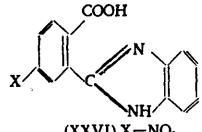


(XXII) X=NH_2;
(XXIII) X=$NHCOCH_3$

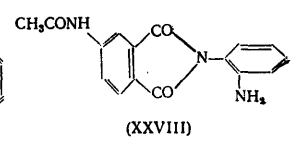
Paper chromatography indicates that six compounds are formed by the interaction of 4-acetamidophthalic anhydride and *o*-phenylenediamine, but of these only 4-acetamido--*N*-*o*-aminophenylphthalimide (XXVIII) could be isolated. From a chromatographic comparison of the reaction products with known specimens, the structure 4-amino--1,2-bisbenzimidazol-2'-ylbenzene (XVII) was assigned to the compound having Rf = 0.6 and yellow fluorescence, the structure of its *N*-acetyl derivative (XVIII) to the compound having Rf = 0.62 and green fluorescence, and the structure of 4-amino-2-benzimidazol-2'-ylbenzoic acid (XXVII) to the compound having Rf = 0.89.



(XXIV) X=NO_2
(XXV) X=$NHCOCN_3$



(XXVI) X=NO_2
(XXVII) X=NH_2

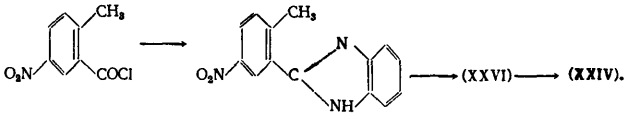


(XXVIII)

Comparison of the ultraviolet spectrum of 1,2-(6'-acetamidobenz-1',2'-oylene)benzimidazole (VIII), prepared by

reducing the 6′-nitro-derivative (VII), with that of the 3′-acetamido-derivative (XXIII) has demonstrated unequivocally that the nitro-group and the acetamido-group exert differently directed effects on the reaction of *o*-phenylenediamine with the corresponding substituted phthalic anhydrides.

The structure of 1,2-(4′-nitrobenz-1′,2′-oylene)benzimidazole is supported by the difference between its ultraviolet spectrum and that of the 5′-nitro-derivative (XXIV), synthesised by the scheme

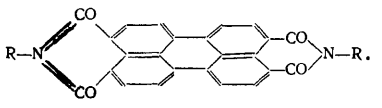


Reaction of 3- and 4-nitrophthalic anhydrides with *o*-phenylenediamine leads to the formation of intermediate products, which on subsequent treatment give 6′- and 4′-nitro-1,2-benz-1′,2′-oylenebenzimidazole (VII) and (XIII) respectively. The acetamido-group, on the other hand, yields the opposite results, reaction of 3- and 4-acetamidophthalic anhydride with *o*-phenylenediamine giving 1,2-(3′-aminobenz-1′,2′-oylene)benzimidazole (XXII) and 4-amino-2-benzimidazol-2′-ylbenzoic acid (XXVII).

X. DYES BASED ON PERYLENE-3,4,9,10-TETRACARBOXYLIC ACID

Perylene-3,4,9,10-tetracarboxylic acid does not, on reaction with *ortho*-diamines, form compounds having desirable dyeing properties. With aliphatic and aromatic monoamines, however, interesting red dyes are obtained, which can be applied as vat dyes[137-139] or pigments[140].

Among vat dyes are known Indanthren Red 2G (R = CH_3) and Indanthren Scarlet R (R = *p*-$CH_3OC_6H_4$).



Brilliant red vat dyes are obtained by introducing other vattable groups into the molecule[141,142]. Small changes in shade can be achieved by also introducing substituents into the dye, e.g. by chlorination or nitration[143,144].

The only dyes which differ in colour from the wide range of red dyes are those obtained by the reaction of perylene-3,4,9,10-tetracarboxylic acid with acrylonitrile and with aminopropionitrile, which are very good grey vat dyes[145].

A well-known pigment used for the colouring of plastics, especially poly(vinyl chloride)[140], is PV Fast Red B,[146] the bis-3,5-dimethylphenylimide of perylenetetracarboxylic acid, which is used for the mass coloration of poly(vinyl chloride)[140] and polyamides. It is employed under the name Permanent Red B Extra[147] for oil varnishes and cellulose nitrate varnishes.

XI. DYES BASED ON VARIOUS DICARBOXYLIC ACIDS

Mainly browns have been obtained from other carboxylic acids which are capable of giving aroyleneimidazole dyes with *ortho*-diamines. The patent literature gives many such examples, but it is most likely that none of these dyes has yet been produced on an industrial scale. The most promising representatives of this group are dyes based on benzanthrone-3,4-dicarboxylic[148] and anthraquinone-2,3-dicarboxylic[125,149,150] acids. Dyes obtained from these acids can apparently be applied as vat and disperse dyes.

XII. REACTIVE AROYLENEIMIDAZOLE DYES

Reactive yellow and red dyes have been obtained by reaction with cyanuryl chloride of both vattable and non-vattable aroyleneimidazoles of the naphthalene and perylene series containing an amino-group[126,127].

XIII. AROYLENEIMIDAZOLE DYES FORMED ON THE FIBRE

In 1956 a process was patented for producing aroyleneimidazole dyes directly on the fibre[151]. A di- or tetracarboxylic acid is mixed with a diamine and a substance which will promote the reaction (a relatively non-volatile organic acid, e.g. lactic acid), the resulting paste is printed on cotton cloth, and the dye is developed by steaming the cloth or heating it to 120–130°.

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CATALYTIC METHODS OF PREPARING ALIPHATIC AND ALICYCLIC AMINES

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I. INTRODUCTION

The chemistry of amines has long attracted the attention of research workers. In particular there are numerous papers on the chemistry of the aromatic amines, but during the past decade more and more papers on the aliphatic and alicyclic amines and on catalytic methods of synthesising them have appeared. These compounds have been the object not only of theoretical investigations but also of a number of investigations connected with the solution of important scientific and technical problems. Information on the aliphatic and alicyclic amines has not been unified and there are no review papers on this important branch of chemistry in recent literature. The well known review paper of Emerson[1] appeared in 1949 and, of course, does not contain material published later.

Aliphatic amines were first discovered by Würtz in 1849 [2] in distilling isocyanates with potassium hydroxide:

$$R{-}N{=}C{=}O + 2KOH \longrightarrow RNH_2 + K_2CO_3.$$

At present there are a number of general and particular methods of synthesising amines. Catalytic methods are the most widely used. The methods are very diverse both with regard to the starting materials and to the catalysts employed; by changing the reaction conditions the yield of primary, secondary, and tertiary amine can be altered as required. Alcohols, ethers, halogen derivatives, aldehydes, ketones, nitrogen-containing compounds, and unsaturated hydrocarbons are used as starting materials for the synthesis of amines. Catalysts have been proposed with the aid of which some amines may be converted into others. Because of the extensive literature on this problem, we considered it expedient to deal only with problems connected with amines proper and not consider amino-derivatives with other functional groups.

Amines are produced in large tonnages by the basic organic synthesis industry. They are used in the production of plastics, explosives, dyes, artificial fibres, and in a number of other branches of industry. For example, vinylamines are used as inhibitors in the polymerisation of vinyl acetylene [3] and also as accelerators in vulcanisation [4] and in the dyeing of polyacrylic fibres [5]. Primary, secondary and tertiary amines are used as addition compounds with boranes in the reduction of organic compounds [6]. Secondary aliphatic amines are used in the synthesis of enamines, the polymerisation and copolymerisation of which yield auxiliary materials used in the textile industry and in the production of plastics [7]. Some higher primary amines, for example, palmitylamine and stearylamine, give auxiliary materials for the textile industry when condensed with hydroxymethylamides [8]. Primary and secondary aliphatic amines are used for the preparation of aminoacroleins [9]. Aliphatic amines with 2 to 20 carbon atoms in the molecule are used as additives to bind metallic impurities in the distillation of alcohols obtained by the hydroformylation of alkenes and subsequent reduction of the aldehydes formed by hydrogen on a nickel catalyst [10]. In connection with reports that some high-molecular primary alkylamines suppress the development of the tubercule bacillus, 1-aminododecane, 2-aminotridecane, and 3-aminotridecane have been synthesised and show the maximum activity *in vitro* [11]. It has been shown that primary amines containing no more than five carbon atoms in the molecule ignite on mixing rapidly with highly concentrated nitric acid and can be used as fuel for liquid reaction engines; branching of the hydrocarbon chain in the amine molecule reduces the rate of ignition [that is, increases the ignition delay (Ed. of Translation)]; on the other hand, an increase in the number of alkyl groups attached to the amino-group increases it. A solution of triethylamine in 2,6-xylidine was used by the Germans under the name "Tonka 250" as a fuel for rocket engines. A mixture of stereoisomeric 2,7-diaminooctanes is used for the preparation of polyamides from adipic acid. In the polycondensation, polyamides with a molecular weight of ~ 50 000 are formed [12]. The secondary diamines

$$C_2H_5NHCR_2(CH_2)_n\,CR_2NHC_2H_5$$

(where R = CH_3 or C_2H_5 and n = 2–7) have been synthesised for tests of ganglionolytic activity; the greatest activity is found when n = 4 and R = C_2H_5. [13] Aliphatic amines of the type $(CH_3)_2NH$ etc. are used for the synthesis of some ethanolamines with spasmolytic properties. For example,