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N-Vinyl Compounds of the Pyrrole Series

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The review deals with the methods of synthesis and reactivities of *N*-vinyl derivatives of pyrrole, indole, and carbazole. Their chemical properties have been compared with one another and also with those of aryl vinyl ethers and enamines. Since the reactions of *N*-vinyl pyrroles have been inadequately investigated, all the principal chemical properties of this series will be considered—mainly with *N*-vinylindole as an example, this compound having been most thoroughly investigated by the authors of the review. The bibliography includes 201 references.

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I. INTRODUCTION

Heterocyclic compounds containing a nitrogen atom in the ring are extremely widely distributed in nature as alkaloids, vitamins, and pigments, and play a very important role in biological processes [1,2]. Many compounds with an indole ring exhibit high pharmacological activity [3].

In recent years unsaturated *N*-heterocyclic compounds have been attracting attention because of their high and unusual reactivity. The vinyl derivatives of pyrrolidone and various other lactams are already used in the plastic and synthetic fibres industry, electronic engineering, and medicine and have been frequently described [4,5]. Among the *N*-vinyl compounds, *N*-vinylindole remained completely uninvestigated for a long time. The introduction into the indole molecule of a vinyl group conjugated via the nitrogen atom with the π-electrons of the double bonds of the benzopyrrole system opens up a path to the synthesis of more complex compounds, including macromolecular compounds. This gives rise to great potential possibilities for the synthesis of new antimicrobial and medicinal preparations, organic semiconductors, and thermally and electrically insulating coatings.

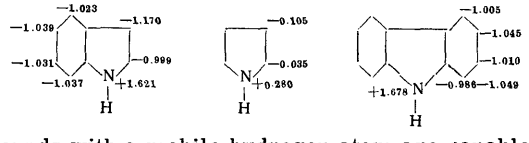
The information in the literature about the chemistry of the parent compound of this series, *N*-vinylpyrrole, is very limited. Only the problem of the preparation and polymerisation of *N*-vinylcarbazole is discussed. Furthermore, the available published data on the *N*-vinyl compounds of pyrrole and its benzo-derivatives have not so far been compiled.

II. METHODS OF SYNTHESIS OF *N*-VINYLPYRROLES

Vinyl derivatives of nitrogen-containing heterocycles may be synthesised in different ways. The methods for their preparation can be divided into several groups in accordance with the reaction on which their synthesis is based: (1) direct vinylation; (2) dehydration of β-hydroxyethyl derivatives of heterocycles; (3) dehydrohalogenation of halogenoethyl derivatives of heterocycles.

1. Direct Vinylation

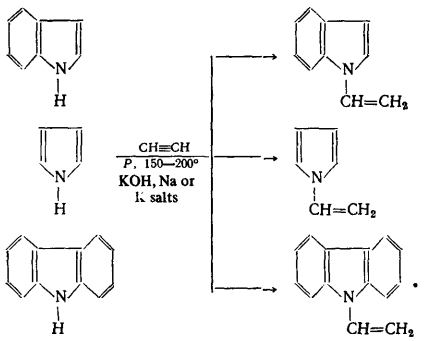
As a result of π-electron conjugation, the electron density at the nitrogen atom in pyrrole, indole, and carbazole molecules is transferred to the ring, which leads to considerable polarisation of the N–H bond. This effect may be regarded as the main reason for the enhanced mobility of the hydrogen atom attached to the nitrogen atom. Recent theoretical calculations confirmed the presence of an excess positive charge at the nitrogen atom of pyrrole systems [1,6]:



Compounds with a mobile hydrogen atom are capable of interacting with acetylene to form vinyl derivatives [7]. The vinylation reaction is based on the work of Favorskii [8], who showed that alcohols add to substituted acetylenes with formation of vinyl ethers. Shostakovskii [9], Prilezhaeva [10], Kalabina [11], and Sidel'kovskaya [12,13] extended this reaction to mercaptans, phenols, lactams, and thiono-amides. Foreign studies in this field have been carried out by German chemists led by Reppe [14,15] and a number of American [16,17] and Japanese [18,19] scientists.

The available literature data show that the vinylation of amino-compounds is more complex than that of alcohols, phenols, and mercaptans. Recently Chekulaeva [20] reviewed the information about the reactions of acetylene with amines and ammonia and described the principal laws governing these reactions. Primary and secondary aliphatic amines react with acetylene in the presence of alkalis, forming resins [14]. The replacement of alkali by zinc or cadmium salts leads to the synthesis of unstable vinylamines [15,20]. Stable products are obtained when heterocyclic imino-compounds are vinylated. The methods of their preparation have been described systematically in individual sections of review articles [14–16,21–23] and also in monographs [5,24].

Usually the interaction of compounds of the pyrrole series with acetylene takes place at elevated temperatures and a pressure of 15–20 atm in the presence of basic catalysts. The latter are alkali metal salts of the compounds vinylated and also substances which are capable of substituting by an alkali metal the hydrogen of the imino-group in the pyrrole molecule:



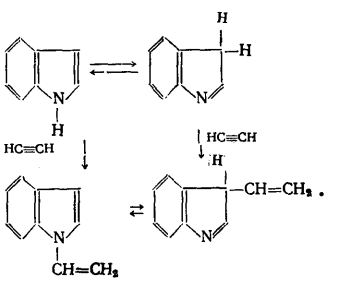
Sodium and potassium hydroxides or alkoxides are frequently employed [15,25] and alkali metals less so [26]. The catalyst is also treated with promoting agents, which make it possible to carry out the reaction at lower pressures and temperatures, accelerate the main vinylation process, and increase the yield. Agents of this kind which have been employed are zinc oxides [27,28], powdered zinc [29,30], and zinc carbonate, phosphate, and sulphide [31]. Sometimes small amounts of ammonia, pyridine, or quinoline are added to the reaction mixture in order to accelerate the reaction [31,32]. The catalyst usually consists of three parts of potassium hydroxide and one part of zinc oxide and is added in an amount of 3–4%. The reaction is normally performed in solution or in suspension. It is very important to carry out the process in an organic solvent which dissolves the vinylated compound, for example benzene, toluene, cyclohexane, methylcyclohexane, decalin, and dimethylcyclohexanol [33]. Acetylene is diluted with nitrogen, carbon dioxide, or methane in proportions of 2 : 1. The reaction lasts 4–5 h. Carbazole is also vinylated at 180°C in the presence of sodamide and calcium carbide in ligroin [34]. *N*-vinylcarbazole is synthesised in high yields at 200°C in ethyl vinyl ether solution [35].

In the reaction of an equimolar mixture of technical fluorine and carbazole with acetylene at a pressure of 39 atm and 195°C in toluene in the presence of potassium hydroxide and added quinoline, Karpukhin and Levchenko [36,37] obtained in 61% yield a mixture of vinyl derivatives containing 45% of *N*-vinylcarbazole.

Pyrrole and its benzo-derivative are also vinylated in the gas phase at atmospheric pressure and a temperature of 250–320°C, but the yield of products is much lower than in the vinylation in the aqueous phase [38,39]. Pyrrole vapour has been vinylated with acetylene over the Fe/K_2CO_3 catalyst at 300°C and a pressure of 300–500 mm. [15] In 1962 a new method was proposed for the synthesis of *N*-vinylpyrrole [40] by allowing gaseous acetylene and pyrrole to come into contact at 150–350°C with a catalyst consisting of an MgO carrier impregnated with 5–15% KOH.

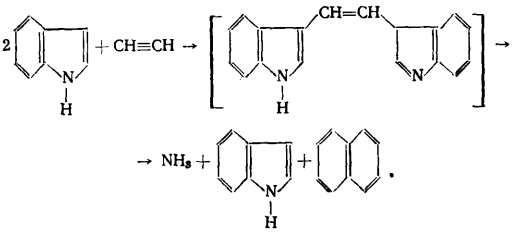
The information about the synthesis of *N*-vinylindole is very limited. Indirect indications of the possibility of the preparation of *N*-vinylindole by analogy with *N*-vinylcarbazole and *N*-vinylpyrrole appeared for the first time in the 1930's in a number of patents [29,28,41]. Reppe [27] describes the synthesis of *N*-vinylindole by the reaction of indole with acetylene under pressure in the presence of 2% KOH at 150–160°C for 70 h. In the 1950's Kawasaki [42] noted that an increase in the amount of KOH and of temperature to 180°C and the use of a potassium salt of indole instead of potassium hydroxide reduces the duration of heating to 4–5 h. *N*-Vinylindole was also synthesised by passing a mixture of indole and acetylene vapours over an iron catalyst at 300°C. [15]

Shostakovskii et al. [43], who studied the vinylation of indole, showed that this is a complex process, since under the conditions of this reaction not only indole itself but also its tautomeric form—pseudoindole—can exist. Nowadays it is no longer surprising that indole and pyrrole are protonated both at nitrogen and carbon. This is indicated by preliminary data obtained in the study of the ionisation of these compounds [44]. One cannot exclude the possibility that both tautomeric forms of indole, which have active hydrogen atoms in positions 1 and 3, can react with acetylene to form *N*-vinylindole and pseudovinylindole by the mechanism



The latter is probably formed as a result of the migration of the vinyl group in the *N*-vinylindole molecule under the conditions of the reaction.

Shostakovskii et al. [43] assumed that the high-boiling compound which they isolated is formed as a result of the interaction of both tautomeric forms of indole with an acetylene molecule. On heating it decomposes into ammonia, indole, and naphthalene:

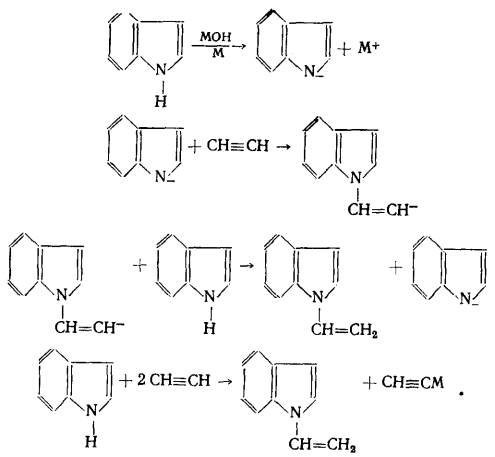


Later Domnina, Skvortsova, and coworkers investigated the reaction of indole with acetylene under pressure in order to drive the reaction towards the optimum degree of formation of one of the tautomeric forms—*N*-vinylindole. They showed that the yield of the latter compound is significantly improved when the reaction is carried out in toluene or dioxan with small amounts of water (about 10%). The solvent favours the ionisation of the initial component and an increase of the concentration of acetylene in the reaction mixture. Potassium hydroxide (about 30%) and sodium hydroxide have been recommended as catalysts [45]. The variation of the yield of *N*-vinylindole with the concentration of potassium hydroxide, the amount of water, temperature, and the duration of the vinylation of indole has been investigated [46]. A decrease of the concentration of potassium hydroxide to 25% lowers the yield of *N*-vinylindole almost by a factor of two. Heating above 220°C leads to thermal polymerisation of the vinylation product. The best result, with the yield of *N*-vinylindole reaching 90% of theoretical, was achieved when indole was allowed

to react with acetylene at 180°C in the presence of 5.5% of metallic potassium [47]. The process takes 30 min. An increase of the duration of the reaction leads to enhanced tar formation.

When the potassium salt of indole is used as a catalyst, the vinylation takes place under the same conditions, the yield of *N*-vinylation reaching up to 88%. The replacement of potassium hydroxide by metals (sodium, lithium, and their salts) proved to be less effective, since the process had to be carried out at a higher temperature (up to 220°C), which results in the polymerisation of the *N*-vinylindole formed.

By analogy with other cyclic imines [48], the mechanism of the vinylation of indole can be represented as follows:



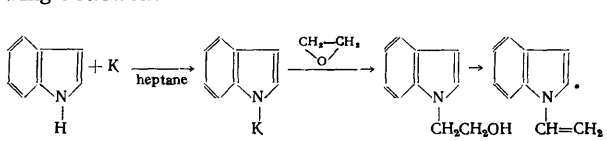
This is confirmed by the synthesis of *N*-vinylindole from potassium indolate when the latter reacts directly with acetylene.

The method of synthesis of *N*-vinyl derivatives of the pyrrole series by direct vinylation has many advantages: the process consists of a single stage, the yields are high, and in many cases the starting material is readily available. However, experiments at elevated pressures and temperatures are complicated by the risk of explosion of acetylene. Therefore in many countries other methods for the introduction of the vinyl group into heterocyclic compounds are being developed together with studies designed to widen the scope of the syntheses based on acetylene, and these are considered below.

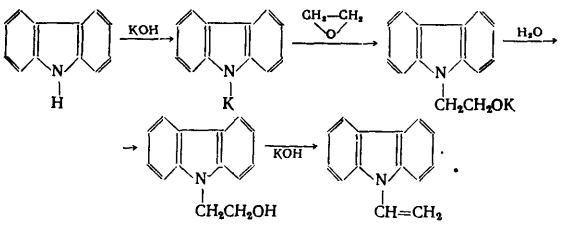
2. Dehydration of β-Hydroxyethyl Derivatives of Heterocyclic Compounds

Carbazole derivatives are dehydrated at a reduced pressure and an elevated temperature, frequently in the presence of potassium hydroxide. In a few cases acid catalysts are employed (potassium hydrogen sulphate, sulphuric acid, acetic anhydride, or alumina).

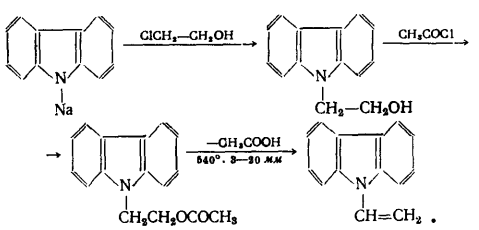
Japanese investigators [49] synthesised *N*-vinylindole from potassium indolate and epoxyethane in 40.5% yield by the following reaction:



They obtained *N*-vinylpyrrole similarly in 23.6% yield. Other workers [50-52] synthesised *N*-vinylcarbazole by the dehydration of *N*-(β-hydroxyethyl)carbazole using the reaction



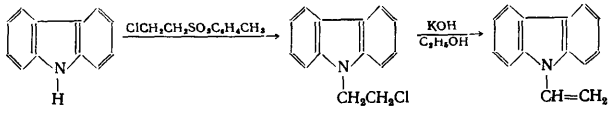
Sometimes the sodium salt of carbazole is used instead of the potassium salt [50,53]. The hydroxy-derivative obtained from the salt and ethylenechlorohydrin is treated with an excess of acetic acid, acetyl chloride, or acetic anhydride and then pyrolysis of the resulting acetate yields *N*-vinylcarbazole:



Lopatinskii et al. [54] obtained *N*-vinylcarbazole in 70–75% yield by the dehydration of *N*-(β-hydroxyethyl)carbazole with 10% potassium hydroxide at 250–270°C. In order to obtain β-hydroxyethyl derivatives, they also used the interaction of halogenocarbazoles with epoxyethane [55,56]. In a recently proposed method [57] *N*-vinylcarbazole and its 3-chloro- and nitro-derivatives are synthesised by the vacuum pyrolysis of the corresponding *N*-(α-acetoxyethyl)-carbazoles, which are readily obtained by the addition of vinyl acetate to carbazoles in solution in aliphatic ketones in the cold in the presence of solid alkalis [58]. The process can be carried out in a single stage without the isolation of the intermediates. The yields of *N*-vinylcarbazoles reach 65–80% of theoretical [59]. In its efficiency the method surpasses all other known methods for the preparation of 3-chloro-*N*-vinylcarbazoles.

3. Dehydrohalogenation of Halogenoethyl Derivatives of Heterocyclic Compounds

The elimination of hydrogen halides from the corresponding α- and β-halogenoethyl derivatives of nitrogen-containing heterocycles is achieved by the action of bases (potassium hydroxide, sodium ethoxide and methoxide, pyridine, sodamide, trimethylamine). Clemo and Perkin [60] obtained *N*-vinylcarbazole and *N*-vinyl-1,2,3,4-tetrahydrocarbazole by the elimination of hydrogen chloride from *N*-(β-chloroethyl)carbazole with alcoholic alkali at 50–60°C:



N-(β-chloroethyl)carbazole is synthesised by the reaction of β-chloroethyl *p*-toluenesulphonate with carbazole in acetone solution in the presence of alkali.

Lopatinskii and Zherebtsov[61] discovered the conditions for the conversion of 3-chloro-, 3,6-dichloro-, 3-bromo-, and 3,6-dibromo-carbazoles into the corresponding *N*-vinyl derivatives. Initially they substituted the hydroxyl in 3-chloro-*N*-(β-hydroxyethyl)carbazole by chlorine using phosphorus pentachloride and then dehydrochlorinated the product by the method described above[60].

Certain other procedures are also used to synthesise *N*-vinyl heterocyclic derivatives. Thus it has been stated that *N*-vinyl derivatives are formed when indole and carbazole react with vinyl acetate in solution in aliphatic ketones in the presence of mercury sulphate and sulphuric acid[62,63]. Unfortunately, however, the resulting vinyl compounds are polymerised under the reaction conditions.

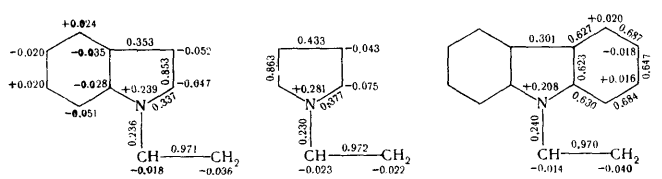
The introduction of a vinyl group into the carbazole molecule by the reaction of the potassium salt of carbazole with vinyl chloride in dimethylcyclohexane under pressure was described as early as the 1930's.[15,64,65]

III. CHEMICAL PROPERTIES OF *N*-VINYLPYRROLES

Although the molecules of *N*-vinyl derivatives of pyrroles and benzopyrroles contain many reaction centres, the chemistry of these compounds has so far been little investigated. For a long time attention was concentrated in the literature solely on the study of the polymerisation of *N*-vinylcarbazole, whereby it is possible to obtain products with valuable properties.

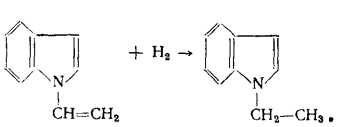
1. Addition Reactions at the Double Bond of *N*-vinylpyrroles

Quantum-mechanical calculations using the semi-empirical self-consistent field MO-LCAO method by Frolov and Kontarev[66,67] showed the following distribution of electron density in the molecules of vinyl derivatives of pyrrole, indole, and carbazole:



The molecular diagrams indicate an increase in the π-electron density at the β-carbon atom of the vinyl group and also at the C_2–C_3 bond of the pyrrole ring. According to modern theoretical concepts, the addition of electrophilic agents to the β-carbon atom of the vinyl group is due to the positive mesomeric and electromeric effects of the imino-nitrogen.

Addition of hydrogen. In the presence of Raney nickel in an alcoholic medium at room temperature and atmospheric pressure *N*-vinylindole readily adds hydrogen to the double bond of the vinyl group, forming *N*-ethylindole[46], the yield of which reaches 80–90%:



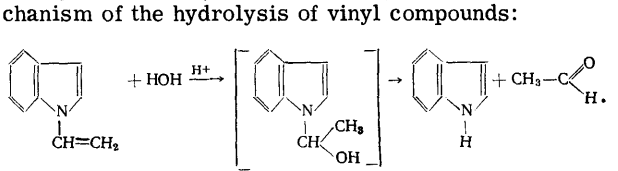
Kawasaki[42] hydrogenated *N*-vinylindole in the presence of the palladium/charcoal catalyst.

N-vinylcarbazole is also readily hydrogenated to *N*-ethylcarbazole[16]. Reppe[15] carried out this process in methanol in the presence of Raney nickel at 80°C and a hydrogen pressure of 15 atm.

Hydrolysis. Like *N*-vinyl-lactams[68], *N*-vinylimides[69,70], and vinylethers[71], *N*-vinylpyrroles are split by mineral acids at the C–N bond with formation of acetaldehyde and pyrroles. Comparison of the literature data[68–71] shows that the hydrolysis of *N*-vinylcarbazole is more difficult than that of *N*-vinyl-lactams and vinyl ethers. The hydrolysis of *N*-vinylcarbazoles requires longer heating and a higher concentration of catalysts. Furthermore, the process is accompanied by side reactions which made it impossible for a long time to isolate the acetaldehyde produced in the reaction, since it immediately interacts with the carbazole to give a crystalline product of unknown structure[60]. When hydrazine hydrate is added to the initial reaction mixture, the hydrolysis goes to completion and acetaldehyde hydrazone is formed almost quantitatively[5]

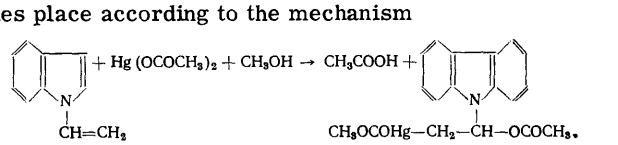
By hydrolysing *N*-vinylcarbazole for four days in a 9 : 1 mixture of methanol and water in the presence of iron(III) nitrate, it proved possible to isolate[72] carbazole and acetaldehyde, identified as the 2,4-dinitrophenylhydrazone. The reaction is accompanied by the formation of 20% of *trans*-1,2-dicarbazolylcyclobutane; the mechanism of this process has been discussed[72].

Shostakovskii et al.[73] investigated the acid hydrolysis of *N*-vinylindole. By varying the concentration of sulphuric acid, temperature, and the duration of reaction, they found that *N*-vinylindole is hydrolysed most completely (to the extent of 97–98%) after 30 h at 60°C in the presence of 4% H_2SO_4. In the presence of a more dilute acid (0.5–3%) the degree of hydrolysis at 30°C did not exceed 15–16%. Shostakovskii et al.[73] suggest that the hydrolysis of *N*-vinylindole proceeds according to the following mechanism, which is analogous to the general mechanism of the hydrolysis of vinyl compounds:



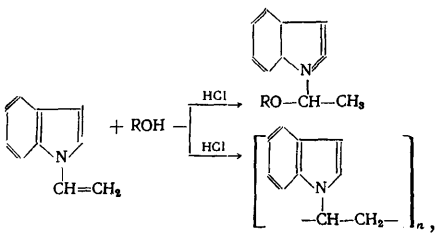
In contrast to *N*-vinylcarbazole, in this case the formation of by-products was not observed; *N*-vinylindole is much more difficult to hydrolyse than alkyl vinyl ethers and *N*-vinyl-lactams[7,74]. However, it is hydrolysed at a lower temperature than aryl vinyl ether. *N*-vinylindole is stable when heated for a long time in dilute alkalis.

Addition of alcohols. Of the reactions involving addition to *N*-vinylcarbazole by a polar mechanism, the interaction of this compound with mercury acetate, which is used for the analytical determination of the monomer, has been described[75]. In absolute methanol the addition takes place according to the mechanism



Skvortsova et al.[76] showed that two competing reactions occur in the interaction of *N*-vinylindole with aliphatic alcohols, phenols, and monocarboxylic acids. The addition of an alcohol to the vinyl group of *N*-vinylindole is accompanied by its homopolymerisation. The alcohols

add in accordance with the Markovnikov rule and the results of quantum-mechanical calculations:

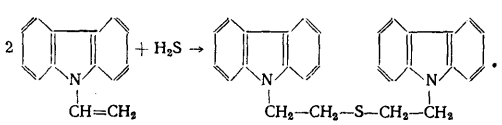


where R = CH_3, C_2H_5, C_3H_7, C_4H_9, or C_6H_5.

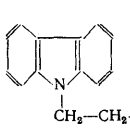
Depending on the reaction temperature, the order of addition of the components, and the nature of the hydroxy-compound, one or other process predominates. It has been established that methanol, ethanol, and propanol react with *N*-vinylindole at temperatures ranging from −7° to +5°C with formation of *N*-α-(methoxy-, ethoxy-, propoxy-)-ethylindoles, their yields reaching 66–74%. C_4 and higher alcohols and also phenols do not add to *N*-vinylindole, since under the reaction conditions (18–20°C) the polymerisation of this compound predominates. It proved impossible to acylate *N*-vinylindole at the double bond of the vinyl group by acids such as formic, acetic, butyric, isobutyric, and valeric. Depending on the strength of the initial acid, *N*-vinylindole polymerises instantly or after several hours.

Addition of thiols. Shostakovskii et al.[77–80] made a detailed study of the thiolation of alkyl vinyl and aryl vinyl ethers and *N*-vinyl-lactams. In her review Prilezhaeva[81] states that the addition of hydrogen sulphide and mercaptans to αβ-unsaturated compounds in the presence of free radical initiators is accompanied by the formation of β-addition products.

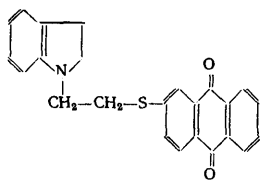
The addition of hydrogen sulphide to *N*-vinylpyrroles is also contrary to the Markovnikov rule[15,16]. Reppe and Nikolai[82,83] obtained di-β-(*N*-carbazolyl)ethyl sulphide by passing hydrogen sulphide into an alcoholic solution of *N*-vinylcarbazole heated to 75°C and containing a small amount of potassium hydroxide:



They synthesised di-β-(1-indolyl)ethyl sulphide by the action of hydrogen sulphide at 80°C on a solution of *N*-vinylindole in butanol in the presence of metallic potassium in an amount of about 0.1%. The reaction of *N*-vinylcarbazole with methane-, ethane-, butane-, dodecane-, and toluene-thiols, thiophenol, thiocresol, chlorothioxylene, thionaphthol, 1- or 2-mercaptoanthraquinone, thioresorcinol, and mercaptobenzothiazole is anomalous[82]. Thus, when thiocresol is refluxed with *N*-vinylcarbazole in a fairly dilute alcoholic solution for 12 h, β-(*N*-carbazolyl)ethylthio-*p*-toluene is formed in the absence of a catalyst:

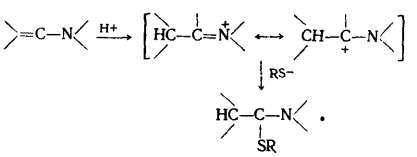


2-Mercaptoanthraquinone reacts with *N*-vinylcarbazole to form 2-anthraquinonylthio-1-(*N*-carbazyl)ethane:

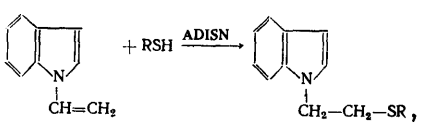


The possibility of an analogous interaction of *N*-vinylpyrrole with hydrogen sulphide and mercaptans to form β-addition products is indicated in patents[82,83], but concrete examples with description of reaction conditions are not given.

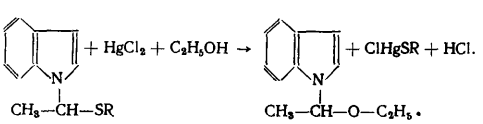
Investigations in recent years showed that certain *N*-vinyl compounds combine with mercaptans in accordance with the Markovnikov rule even under the influence of radical initiators (as in their absence). Leonard and Hay[84] and Lawesson and coworkers[85] found that cyclic enamines interact with mercaptans, forming α-addition products:



Shostakovskii et al.[86] developed a method for the preparation of new sulphur compounds of the indole series consisting in the interaction of *N*-vinylindole with mercaptans. They showed that free-radical addition of thiols to *N*-vinylindole under the influence of azodi(isobutyronitrile) (ADISN) takes place mainly with formation of *N*-(β-alkylthioethyl)indole (yield 75–80% of theoretical):

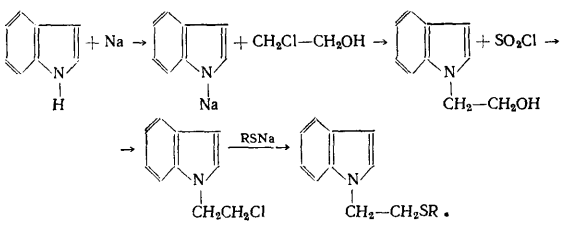


where R = H, C_2H_5, iso-C_3H_7, or t-C_4H_9. Together with this compound, a mixture of α- and β-addition products was isolated. The structure of *N*-(β-ethylthioethyl)indole was demonstrated unambiguously by proton magnetic resonance. Its spectrum consists of four multiplets comprising three triplets (δ = 1.0, 2.57, and 3.96 p.p.m.) and a quartet (δ = 2.14 p.p.m.). The presence of α-addition products is confirmed by the reaction with an alcoholic solution of mercuric chloride[78,87,88]:



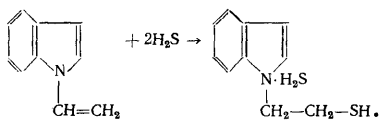
The amount of acid produced from the various alkylthio-derivatives varies from 38 to 95%. The physical constants of *N*-(α-ethoxyethyl)indole isolated from the reaction mixture agree with those of the products of the addition of ethanol to *N*-vinylindole[89,90].

To confirm the structure of the alkylthio-derivatives of *N*-vinylindoles, Domnina [89] attempted an indirect synthesis of the β-addition products by the following process:



Owing to the great tendency of indole derivatives to undergo dimerisation and polymerisation in an acid medium, this synthesis could not be taken to completion [91].

On heating to 80°C in the absence of an initiator, mercaptans do not add to *N*-vinylindole and, when the reaction mixture is distilled, the starting materials are completely recovered. Acidic catalysts, such as sulphur dioxide or *p*-toluenesulphonic acid, also do not facilitate their interaction and at different reaction temperatures only *N*-vinylindole pentamers and hexamers are produced [90]. According to a patent application [82], a sulphide derivative could not be isolated in the reaction of *N*-vinylindole with hydrogen sulphide. It was established that at 80°C *N*-vinylindole interacts with two hydrogen sulphide molecules:

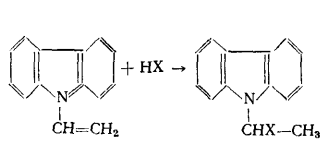


The present authors believe that, by analogy with mercaptans the HS group adds to the β-carbon atom of the vinyl group and the second hydrogen sulphide molecule forms a salt [89].

Halogenation and hydrohalogenation reactions. Studies on the halogenation of *N*-vinyl compounds are limited to only a few examples. The interaction of *N*-vinylcarbazole with bromine is mentioned in Reppe's review [15]. Reppe believes that, in the presence of potassium carbonate at −10°C, *N*-vinylcarbazole reacts with bromine to form methoxybromoethylcarbazole. The structure of the product was not proved. According to a patent [92], *N*-vinylcarbazole polymerises under the action of a small amount of hydrogen chloride.

Pielichowski and coworkers [93,94] recently described the halogenation and hydrohalogenation of *N*-vinylcarbazole. They suggest that bromination with a solution of bromate and bromide involves the vinyl group with formation of a product containing three or six bromine atoms, i.e., together with the addition reaction, hydrogen atoms are also substituted by bromine.

Pielichowski [94] believes that the addition of hydrogen halides to *N*-vinylcarbazole takes place in accordance with the Markovnikov rule, α-halogenoethylcarbazoles being formed:

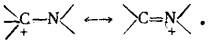


The reaction is carried out in carbon tetrachloride solution, through which hydrogen chloride, bromide, iodide, or fluoride is passed during 1 h. The addition products have the following melting points respectively: 255°, 165°, 165–166°, and 123–125°C. The structure of the chloro-derivatives is confirmed by the fact that they differ in their properties from those of *N*-(β-chloroethyl)-carbazole synthesised earlier by Clemo and Perkin [60].

For a long time there was no information in the literature about the halogenation of *N*-vinylindole. Shostakovskii et al. found that chlorine and bromine react vigorously with *N*-vinylindole in the cold in carbon tetrachloride. By analogy with the hydrogenation of vinyl ethers [7] and also *N*-vinylphthalimide [96] and in agreement with data obtained by elemental analysis, the authors initially suggested that bromine adds to *N*-vinylindole at the vinyl group with formation of *N*-(αβ-dibromoethyl)indole or tribromoethylindole. However, subsequent studies of the halogenation of *N*-vinylindole established that, depending on the relative amounts of the starting components and the duration of interaction, polymeric products with various halogen contents are obtained [66] (for a more detailed description, see p. 415).

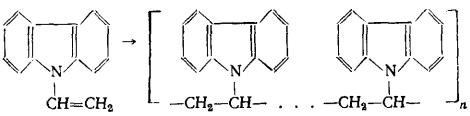
2. Polymerisation

The structure of the group linked to the nitrogen atom strongly influences the activity of *N*-vinyl compounds in polymerisation. Aliphatic vinylamines are known to be inactive in polymerisation. Plesch [97] explains this inertness of the growing chain by the resonance



In vinylcarbazole this difficulty is overcome as a result of the tendency to retain the aromatic properties of the heterocyclic compound. Because of this, *N*-vinylcarbazole is capable of polymerisation on heating above its melting point (85°C) without catalyst [98,99]. *N*-vinylindole also polymerises readily [46].

Among the vinyl monomers of the pyrrole series, *N*-vinylcarbazole has been most thoroughly investigated [15,100–102]. It can be readily polymerised by the usual methods —in the solid state, in solution, in emulsion, and in suspension in the presence of various initiators [103,104]. The reaction leads to the formation of a linear polymer with the following structure:



N-Vinylcarbazole and *N*-vinylindole undergo both cationic and radical polymerisation and therefore differ from vinyl ethers, which polymerise exclusively under the action of acid reagents [7,105–107].

t-Butylperoxide, azodi(isobutyronitrile), and hydrogen peroxide are used as the radical initiators of the block polymerisation of *N*-vinylcarbazole [108–110]. Benzoyl peroxide does not initiate the polymerisation of *N*-vinyl compounds [111]. Alkaline oxidising agents [5], such as sodium peroxide, perborate, and dichromate are catalysts for the radical polymerisation of *N*-vinylcarbazole in suspension. In the presence of 0.005–0.01% of azodi(isobutyronitrile) *N*-vinylcarbazole is converted into an almost colourless high-molecular polymer [112], while in an aqueous dispersion grains 0.5–1 mm in diameter are produced [113]. Organic bases inhibit its polymerisation [114].

The cationic polymerisation of *N*-vinyl compounds of the pyrrole series takes place readily. Boron trifluoride, various metal chlorides such as zinc chloride, aluminium chloride, etc., acid chlorides (sulphuryl, thionyl, acetyl,

and benzoyl chlorides), and halogeno-hydrocarbons are widely used in this case [92,115-118].

The solid-phase polymerisation of *N*-vinylcarbazole in the presence of Friedel–Crafts catalysts yields polymers with a low molecular weight [119]. In liquid sulphur dioxide at temperatures between −10° and −70°C *N*-vinylcarbazole and *N*-vinylpyrrole form polymers with high molecular weights reaching 90 000. [116,117] The reaction takes place by an ionic mechanism with the initial formation of a complex of *N*-vinylcarbazole with sulphur dioxide [120,121]. These products have valuable technical properties, mainly as impregnating materials [122,124].

N-Vinylcarbazole polymerises even in the presence of morpholine [125]. In the search for the synthesis of pure high-molecular polyvinylcarbazole organic compounds such as *p*-chloroaniline [126], various pyrylium salts [127], and also methyl methacrylate (1–10%) have been investigated as initiators [128]. Recently Japanese workers [129] found that *N*-vinylcarbazole polymerises by a cationic mechanism in the presence of electron acceptors such as gaseous chlorine, sulphur dioxide, and maleic anhydride [130,131]. They suggest that the monomer forms with the acceptor a charge-transfer complex, which is a source of cationic radicals with a localised carbonium ion. Such complexes exhibit paramagnetic properties and initiate the polymerisation of *N*-vinylcarbazole.

When electron acceptors such as dichlorodicyanobenzoquinone, *p*-chloranil, dichlorobenzene, and others were employed [49], the polymerisation activity decreased in the series *N*-vinylcarbazole > *N*-vinylindole > *N*-vinylpyrrole.

The anionic-coordination polymerisation of *N*-vinylcarbazole is carried out in the presence of t-C_4H_9Li–$TiCl_4$ Ziegler–Natta catalysts [132]. The maximum yield of the isotactic polymer reaches 80% for the ratio Li : Ti = 1.5 : 1.7.

Polyvinylcarbazole was obtained in 23–100% yield at temperatures between −78° and +80°C when $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$, $TiCl_2(OC_3H_7)_2$, $FeCl_2(OCOCH_3)_2$, and $SnCl_2(OCOCH_3)_2$ were used as catalysts [133].

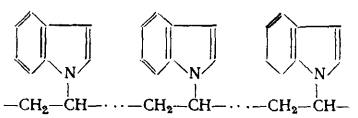
The solid-phase polymerisation of *N*-vinylcarbazole on irradiation with sunlight, ultraviolet light, and γ-rays has been investigated [134–137].

Although the methods for the polymerisation of *N*-vinylcarbazole using all the catalysts enumerated above have been described in many patents, the polymers obtained in this way have not found practical application due to their low molecular weight. The development of the *N*-vinylcarbazole industry in the USA showed that high-molecular weight polymers are mainly manufactured. They are distinguished by their stability to high temperatures and chemical reagents and also by low dielectric constants; such polymers are obtained only by alkaline oxidative polymerisation in emulsion [138]. The process is carried out under a pressure of about 18 atm at 120–180°C. Special initiating agents are potassium or sodium dichromate in an alkaline medium.

Polyvinylcarbazole resins are widely used as surface coatings, for the impregnation of paper, and for the protection of electrical equipment [2].

The information in the literature about the properties and methods of preparation of polyvinylindole is extremely limited. There exist several foreign patents [109,114,116] where the possibility of the polymerisation of *N*-vinylindole is indicated, by analogy with its homologue—*N*-vinylcarbazole. An *N*-vinylindole polymer with a high softening point was obtained by Kawasaki [42] at room temperature in the presence of 4% hydrogen chloride. Schildknecht [100] described the polymerisation of *N*-vinylindole under the influence of 0.01% $BF_3(OC_4H_9)$ below 25°C.

To elucidate the reactivity of the double bond of *N*-vinylindole in polymerisation reactions, Domnina and Skvortsova [139] studied this reaction under the influence of ionic catalysts and free radical initiators. The metal chlorides $SnCl_2.2H_2O$, $SnCl_4$, $AlCl_3$, $TiCl_4$, $TiCl_3$, $FeCl_3$, and also $BF_3O(C_2H_5)_2$ were tested as cationic catalysts. In the presence of 2% $SnCl_4.5H_2O$ *N*-vinylindole polymerises to the extent of 96–98% in 24 h. By analogy with the structural formula of polyvinylcarbazole, it is suggested that the principal unit in polyvinylindole may have the following structure:



The study of the molecular weight distribution in the polymerisation product of *N*-vinylindole by a fractionation procedure showed that polyvinylindole consists mainly of a weakly disperse mixture of polymeric homologues. The maximum on the differential distribution curve is located at low molecular weights, between 700 and 1000, and is fairly broad.

The calculated viscometric constants in the Mark–Houwink equation indicate an extended, rigid, rodlike structure of the polyvinyl molecule and suggest that the latter exhibits electrolytic properties.

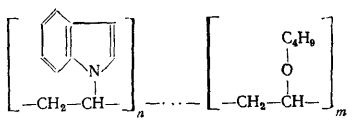
In the presence of benzoyl peroxide *N*-vinylindole does not polymerise, while hydrogen peroxide gives rise to its quantitative conversion into a solid polymeric product. Under the influence of azodi(isobutyronitrile), *N*-vinylindole forms a vitreous substance with a molecular weight in excess of 4000. Thus *N*-vinylindole is an active vinylpolymer capable of polymerising readily both by an ionic and a radical mechanism.

3. Copolymerisation and Activity Constants

Despite the large number of studies dealing with the copolymerisation of unsaturated monomers, so far little work of this kind has been done on the *N*-vinyl compounds of the pyrrole series. There is only one patent [140] which describes a method for the preparation of the copolymer of *N*-vinylpyrrole with tetrachlorodivinylbenzene and acrylonitrile in the presence of organic peroxides. For a long time there were no data whatever about the behaviour of *N*-vinylindole in the copolymerisation reaction.

Shostakovskii et al. [141] studied the free radical copolymerisation of *N*-vinylindole with methyl methacrylate and methacrylic acid. The reaction was carried out with different component ratios in the presence of azodi(isobutyronitrile) at 60°C for 100 h. The resulting copolymers had low molecular weights and a higher relative contents of *N*-vinylindole units than in the mixture of monomers. Potentiometric studies of the copolymers of *N*-vinylindole with methacrylic acid established that they dissociate like acids. The relative activity constants r_1 and r_2 were calculated from the copolymerisation data by a graphical method using the integral equation of Mayo and Lewis. It was found that $r_1 = 1.9 \pm 0.5$ and $r_2 = 0.42 \pm 0.1$ for the monomer pair *N*-vinylindole–methyl methacrylate and $r_1 = 1.43 \pm 0.05$ and $r_2 = 0.096 \pm 0.03$ for the monomer pair *N*-vinylindole–methacrylic acid. These constants confirm that in copolymerisation with methyl methacrylate and methacrylic acid *N*-vinylindole is the more active monomer.

N-Vinylindole retains maximum activity also in the copolymerisation with vinyl ethers. Domnina[89] studied for the first time the copolymerisation of *N*-vinylindole with butyl vinyl ether by ionic and radical mechanisms. Tin, iron, and aluminium chlorides were tested as cationic catalysts. It was shown that, as the amount of *N*-vinylindole in the initial mixture increases, there is an increase in the yield of the copolymer and a decrease in the amount of ether units in the latter. When the *N*-vinylindole : butyl vinyl ether ratio is 20 : 80, both monomers are incorporated in the polymeric chain in approximately equal amounts. Both solid and oily products are then obtained. Spectroscopic and chemical studies suggest the following structure of the principal copolymer units:



where $n > m$. Calculation gives $r_1 = 7.76 \pm 0.58$ for *N*-vinylindole and $r_2 = 0.12 \pm 0.007$ for butyl vinyl ether.

N-Vinylindole is of course the more active in the free radical interaction of these monomers. Thus in copolymerisation initiated by azodi(isobutyronitrile) products with compositions corresponding to component ratios of 90 : 10 and 85 : 15 are formed regardless of the initial component ratio. The low softening points of these copolymers, in the range 350–400°C, and their insolubility in many organic solvents are evidence of their high molecular weight.

Phenyl vinyl ether does not interact with *N*-vinylindole in the presence of cationic catalysts. In this case the polymerisation of each monomer separately takes place. However, phenyl vinyl ether, which does not show a tendency to radical polymerisation, copolymerises with *N*-vinylindole under the action of radical initiators[89].

The behaviour of *N*-vinylcarbazole in copolymerisation reactions has been studied in greater detail and there are more examples. The available literature data on the copolymerisation of *N*-vinylcarbazole with unsaturated hydrocarbons and also with vinyl and acrylic monomers are described below systematically and their practical applications are indicated. Thus polyisobutylene forms with 2% of *N*-vinylcarbazole a rubberlike product[142–149]. It can be vulcanised and, as regards stability to high temperatures, it surpasses polyisobutylene itself. Copolymerisation of *N*-vinylcarbazole with ethylene at 150–300°C under a pressure of 1500 atm in the presence of peroxide catalysts yielded products containing 70–95% of ethylene[146]. Polypropylene is also modified by being mixed with a preformed copolymer of ethylene and *N*-vinylcarbazole[147]. These products are very flexible and highly viscous, have a high tensile strength, and are used as gasket for the protection of glass from cracking. Copolymers of *N*-vinylcarbazole with triphenylethylene have been obtained by solid-state and emulsion polymerisation with peroxide catalysts[148]. *N*-Vinylcarbazole can be copolymerised with vinylphenol by the emulsion method in the presence of 20% H_2O_2 in polyepoxyethane and in the presence of sodium sulphate in sulphonated castor oil[149]. The copolymerisation of *N*-vinylcarbazole with styrenes and a mixture of styrene and acrylonitrile has been investigated in greater detail[33,149–152]. *N*-Vinylcarbazole interacts with styrene in the presence of 0.05–2 parts of alkanethiols and 0.1–10 millimoles of hydroperoxides obtained from di-isopropylbenzene, its halogeno-derivatives, phenylcyclohexane, and an equimolar amount of iron pyrophosphate at 30–40°C.[153] The styrene–*N*-vinylcarbazole copolymers exhibit high thermal stability (127°C) and low dielectric losses (0.00081).[149] Fluorostyrene and 3,4-difluorostyrene form with *N*-vinylcarbazole products which may be used as electrical insulators[154]. In the presence of 0.1% of benzoyl peroxide *N*-vinylcarbazole copolymerises with di(*p*-vinylphenyl)sulphide[155]. The copolymers of *N*-vinylcarbazole and *N*-vinylpyrrolidone[156] are used as stabilisers for hydrazine, fibre-forming compositions, and as adhesives for the improvement of the structure of soils. *N*-Vinylcarbazole forms with acrylonitrile[157,158] polymeric products in the presence of potassium persulphate at 80°C. On irradiation, it reacts with acrylate and methacrylate[159].

The capacity of *N*-vinylcarbazole to copolymerise with other monomers was characterised quantitatively for the first time in 1949 by Alfrey and Kapur[151] in copolymerisation with methyl methacrylate and styrene. Later in 1961 Hart[160] obtained improved values of these characteristics and calculated the specific activity Q and the polarity e.

Table 1. Activity constants for the copolymerisation of *N*-vinylcarbazole (M_1) with certain vinyl monomers (M_2).

M_2	r_1	r_2	Q_1	e_1	Refs.
Methyl methacrylate	0.040	2.0	0.20	−1.20	160
Methyl methacrylate	0.20	2.0	0.25	−0.56	151
Methyl acrylate	0.050	0.50	0.26	−1.32	160
Styrene	0.035	5.7	0.48	−2.07	160
Styrene	0.012	5.5	0.68	−2.45	151
Vinyl chloride	3.7	0.020	3.8	−1.01	160

According to Table 1, the copolymerisation constants show that in reactions with methyl methacrylate and styrene *N*-vinylcarbazole is the less active monomer. The polymeric radical with a terminal *N*-vinylcarbazole unit reacts much more rapidly with methyl methacrylate or styrene than with *N*-vinylcarbazole itself.

Table 2. Copolymerisation constants r_1 and r_2.

M_2	r_1	r_2	$r_1 \cdot r_2$
Vinyl formate	4.220±0.160	0.196±0.004	0.827
Vinyl acetate	3.020±0.240	0.152±0.018	0.465
Vinyl propionate	1.680±0.140	0.076±0.018	0.128
Vinyl butyrate	1.280±0.060	0.059±0.020	0.074

Chernobai et al.[161] made a spectrophotometric study of the copolymers of *N*-vinylcarbazole and methyl methacrylate. Ushakov and Nikolaev[162] studied the copolymerisation of *N*-vinylcarbazole with esters of vinyl alcohol and certain organic acids (formic, acetic, propionic, and butyric) in the presence of 0.5% of benzoyl peroxide. All the systems investigated have been characterised by the copolymerisation constants listed in Table 2.

The calculated copolymerisation constants r_1 and r_2 show that *N*-vinylcarbazole adds to the poly(*N*-vinylcarbazole) radical and to the polymeric chain with a terminal vinyl ester group much more rapidly than the second reaction component.

The experimental data accumulated so far are still insufficient to arrive at reliable conclusions concerning the reactivity of *N*-vinyl compounds of the pyrrole series in copolymerisation as a function of the characteristics of their structure. The number of studies dealing with quantitative calculations of the reactivity is extremely limited even for *N*-vinylcarbazole, the polymers of which are widely used in industry.

IV. CHARGE-TRANSFER COMPLEXES BASED ON PYRROLE, INDOLE, CARBAZOLE, AND THEIR VINYL HALOGEN-CONTAINING DERIVATIVES

The electron-donor properties of the nitrogen atom in the molecules of the heterocyclic compounds are responsible for their capacity to form complexes with various electron acceptors, including iodine, bromine, and chlorine. The study of the problem of intermolecular interaction has developed only recently. Intensive investigation of this problem has been additionally stimulated by the presence of semiconduction in a number of complexes and also by the fact that they can form as intermediates in many complex chemical reactions and biochemical processes [163-167]. The products of intermolecular donor–acceptor interaction are called charge-transfer complexes.

Blyumenfel'd et al. [168] state that such complexes are formed as a result of the redistribution of electron density in the system, leading to a negative charge at the acceptor and a positive charge at the donor. If the degree of transfer of an electron from one molecule to another is slight, the complex is unstable and easily decomposes into the initial molecules. If the interaction is very strong, then redistribution of electron density can lead to complete electron transfer with formation of either an ion pair or of two isolated species.

The theory of intermolecular donor–acceptor interaction was devised as late as the 1960's by Mulliken [169-173], who developed the quantum-mechanical concept of "complex mesomerism" put forward previously by Izmail'skii [174,175]. According to Mulliken's theory, the ground state of the complex is intermediate (mesomeric) between non-ionic and ionic structures, with the former predominating:

$$A + B \rightleftarrows [|\underline{A \ldots B}|] \longleftrightarrow [A^+ \ldots B^-|]$$

Transition to a higher state is accompanied by the appearance of a new intense long-wavelength absorption band, which is frequently the best characteristic of such complexes [176-178].

Aromatic amines and heterocycles with a nitrogen atom, which can be regarded both as π-electron and n-electron donors, constitute an interesting group of donors [179-181]. The study of charge-transfer complexes based on pyrrole compounds has assumed particular importance because they are often constituents of medicinal preparations. Among these compounds, indole derivatives merit most attention. A number of studies carried out by different investigators confirm the electron-donor properties of such compounds. The preparation of complexes of tryptophan or the corresponding indole derivatives with various biochemical electron acceptors containing isoalloxazine or pyridine rings has been described [182-185]. The capacity of indole to form complexes with many electron acceptors such as trinitrobenzene, *p*-benzoquinone, and chloranil is known [186]. A very stable charge-transfer complex of indole and iodine has been described recently [187].

Pullman and Pullman [1], who reviewed studies in quantum biochemistry, state that, judging from the energy coefficient of higher filled molecular orbitals, the electron-donor properties increase on going from pyrrole to indole and remain almost unchanged on going from indole to carbazole. Stable complexes with iodine are formed only by pyrrole and indole. Voronkov et al. [188] investigated by refractometric physicochemical analysis binary systems comprising monosubstituted benzenes of the type C_6H_5X (X = fluorine, chlorine, bromine, or iodine) with simple heterocycles, including pyrrole. They established that they are capable of forming 2 : 1 charge-transfer complexes. The authors concluded that such complexes are formed on the basis of the deviation from additivity of the isotherm and the colour change in the system. Electron transfer reactions with the tropylium cation, carbazole, and *N*-methylcarbazole have been investigated [189].

The studies of charge-transfer complex based on high-molecular-compounds, assumed great importance in the 1960's. [190] Hoegl et al. [190] obtained polymeric complexes based on polyvinyl aromatic, polyvinyl heterocyclic, and other compounds. The methods of their preparation have been described in several German and Belgian patents [191-194]. Hoegl devotes most attention [195,196] to the preparation of complexes based on polyvinylcarbazole. It was established that the latter reacts with nitro-compounds, acids (hydrogen chloride, malonic acid, phthalic acid), esters (dimethyl terephthalate), halogeno-compounds (tetrabromo-*p*-xylene, triphenylchloromethane, 9,10-dichloroanthracene), and quinones (chloranil and bromanil, phenanthrenequinone) [190].

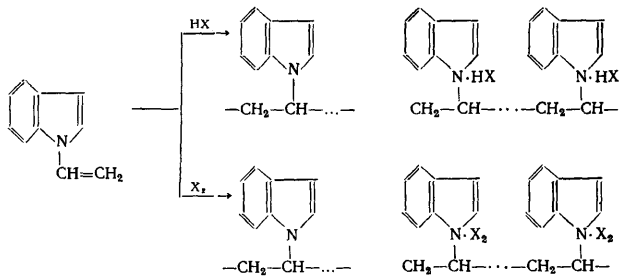
In 1965 Japanese investigators showed that polyvinylcarbazole forms at room temperature in chloroform solution complexes with tetracyanoquinodimethane [197], antimony pentachloride, and iodine [198]. All these products are deeply coloured and absorb in the visible part of the spectrum. Their resistivity is in the range 10^{-12}–10^{-16} Ω^{-1} cm^{-1}.

The solid-phase polymerisation of *N*-vinylcarbazole initiated by charge-transfer complexes of the monomer with acceptors such as Cl_2, Br_2, I_2, $SnCl_4$, and SO_2 is being investigated. Takakura, Okamura, and coworkers [199] made spectroscopic studies of these complexes.

In a more thorough investigation of the halogenation and hydrohalogenation of *N*-vinylindole, Shostakovskii and coworkers [200,201] showed that, instead of the expected products of the addition of the halogen to the double bond of the vinyl group, tetra- and hexamers of the halogeno-derivatives of *N*-vinylindole are mainly formed. It was established that chlorine, bromine, iodine, and the corresponding hydrogen halides readily add to *N*-vinylindole with formation of brightly coloured red, cherry-red, and brown powders which remain stable on storage and are also stable to acid and alkaline hydrolysis. The intense colour, the relatively high molecular weight, the variable composition of the compounds formed, and also the results of quantum-mechanical calculations indicating a relatively low ionisation potential of the *N*-vinylindole molecule led to the hypothesis that polymeric charge-transfer complexes are formed in this case. This is also confirmed by the appearance in the electronic spectra of the halogeno-derivatives of *N*-vinylindole of a broad band with a maximum in the regions 490–500 nm and 350–400 nm.

The fact that all the products of the halogenation and hydrohalogenation of *N*-vinylindole give rise to an ESR signal, which is absent from polyvinylindole, is important evidence for the formation of charge-transfer complexes. The sum of the data obtained suggests that, when halogens

and hydrogen halides react with *N*-vinylindole, the latter undergoes vinyl polymerisation with simultaneous formation of a charge-transfer complex by the following mechanism:



where X = Cl, Br, or I is a σ-electron acceptor component.

According to Mulliken's classification, these complexes may be regarded as the $n\pi\sigma$ type, but in their structure they should also be closer to the $\pi\sigma$ type than to the $n\sigma$ type.

Catalytic amounts of bromine, iodine, chlorine, and the corresponding hydrogen halides initiate the low-molecular polymerisation of *N*-vinylindole and also *N*-vinylcarbazole [121,129,201].

It has been shown that polyvinylindole also readily forms polymeric complexes of the type N...HX and N...X_2 which have a deep colour and give rise to ESR signals [201]. Their resistivity is in the range 10^{-14}–10^{-10} Ω^{-1} cm^{-1}.

Investigations have shown that the halogenation and hydrohalogenation of *N*-vinylindole is a fairly complex process. There are several competing reactions due to the presence in the *N*-vinylindole molecule of several active centres, including the double bond of the vinyl group and the unshared electron pair of the nitrogen atom.

Our earlier hypothesis that bromine adds to the vinyl group [95] appears to be improbable. Probably the same may be said of the work of Pielichowski [93,94], who is also more likely to have dealt with polymeric charge-transfer complexes than with products of the αβ-addition of fluorine, chlorine, bromine, and iodine to *N*-vinylcarbazole.

It follows from the literature data examined that *N*-vinyl compounds of the pyrrole series have been little investigated and are an interesting object for the study of the chemical properties of molecules with several reactive groups.

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