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The reactions of polycarboxylic acid *o*-dinitriles with aromatic diamines

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Abstract. Experimental data on the interaction of phthalodinitriles and bis(phthalodinitriles) with aromatic diamines are surveyed. The dependence of the mechanism of the reaction of phthalodinitriles with diamines on the structure of the diamine and the phthalodinitrile as well as the nature of the reaction medium is examined and general ideas concerning the mechanism of this reaction are formulated. The principal features of the polycondensation of bis(phthalodinitriles) with diamines are specified and the possibility of using this reaction to obtain a series of new classes of heterocyclic polymers with benzopyrrole fragments in the chain is demonstrated. The bibliography includes 70 references.

I. Introduction

A leading aspect of polymer chemistry is the synthesis and study of polyheteroarylenes with a cyclochain structure,[1-7] which have a series of valuable thermal, physicochemical and electrical properties. This review is devoted to a nontraditional approach to the synthesis of heterocyclic polymers, namely the polycondensation of tetracarboxylic acid *o*-dinitriles and aromatic diamines.

Studies on the chemistry of the interaction of *o*-dinitriles of aromatic di- and poly-carboxylic acids with diamines were initiated by the researches of Elvidge and coworkers[8,9] into the condensation of phthalodinitrile with aniline and diamines. Unfortunately, these very interesting reactions did not initially attract the attention of other investigators. It was not until 1967 that Packham and coworkers[10-13] turned their attention to these reactions and attempted to investigate them in greater detail in relation to the interaction of phthalodinitrile with 2,6-diaminopyridine and to use it for the synthesis of polymers with macroheterocycles in the chain. Siegel[14] and Balahura and Purcell[15] studied the mechanism of the condensation of phthalodinitrile with diamines in the presence of metal salts. The condensation of phthalodinitrile with diamines has been used as a preparative method of synthesis of macroheterocyclic compounds.[16,17]

These isolated communications in essence exhaust the studies of the interaction of *o*-dinitriles with the amino-group carried out hitherto.

Studies by Gaumans et al.[18] and Packham and Rackley[19] were devoted to the polycondensation of tetracarboxylic acid tetranitriles and diamines, which results in polymer formation with benzopyrrole fragments in the chain. Fusion of tetracarboxylic acid tetradinitriles with diamines at 300 °C leads to black insoluble and infusible polymers to which a macrocyclic structure has been assigned solely on the basis of IR spectroscopic data.[20] For a long time, there had been no systematic studies whatsoever of the effect of the structure of the starting materials, nature of the reaction medium, and the reaction conditions on the structure and properties of the compounds formed. Clearly, investigation of these problems is essential for the determination of the synthetic possibilities of the reaction, the elucidation of the reaction mechanisms occurring in the interaction of phthalodinitriles and tetracarboxylic acid tetranitriles with diamines, and the determination of the general characteristics of the process.

The few literature data on the model reaction of phthalodinitrile with aromatic diamines,[11,14,15] show that polycondensation of aromatic tetracarboxylic acid tetranitriles with aromatic diamines is an extremely complex process, which may lead to the formation of macrocyclic polymers, polymers without macrocycles, as well as polymers with a mixed structure. Therefore, in order to be able to specify the reaction, it was first essential to investigate in detail the main features of the condensation of phthalodinitriles with aromatic diamines. The macroheterocyclic compounds formed under these conditions in a number of instances were called hexazocyclanes, and polymers containing macroheterocycles with the corresponding structure in the chain were called polyhexazocyclanes.[7,21]

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II. Interaction of phthalodinitrile with aromatic diamines

From literature data,[22,23] one may postulate that, when the condensation is carried out in an alcoholic medium, diamines react not with phthalodinitrile but with the product of its interaction with alcohol — 1-alkoxy-3-iminoisoindole. We studied the role of the hydroxylated solvent, and hence also the structure of the 1-alkoxy-3-iminoisoindole on the composition of the products of the condensation reaction between phthalodinitrile and *p*-phenylenediamine.[7,21,24-26] Butyl alcohol, cyclohexanol, phenol, and its derivatives with electron-donating substituents (cresols, dimethylphenol) and electron-accepting substituents (chloro-, bromo-, nitro-, and methoxy-phenols) were used as the reaction medium. The reaction products were investigated by the mass spectrometry and thin-layer chromatography (TLC) with the use of reference substances synthesised by specially developed methods. The results made it possible to put forward mechanisms of the condensation of phthalodinitrile with *p*-phenylenediamine in solvents of different nature.

Thus it was found that chloro- and nitrophenols function not only as the reaction medium but also as one of the reactants and enter into the composition of the reaction products (Scheme 1).

The condensation products of phthalodinitrile with *p*-phenylenediamine in aliphatic and alicyclic alcohols contain a wide range of compounds in which the content of the macroheterocycles **1** is only 50% (Scheme 2).

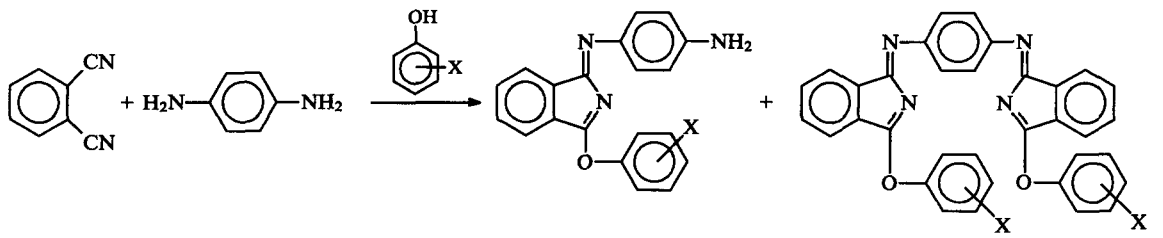
In the reaction of phthalodinitrile with *p*-phenylenediamine in phenol and its derivatives with electron-donating substituents, the yield of the macroheterocycle increases to 85%. The process is extremely selective and, apart from the macroheterocycle **1**, only compound **2** was found among the reaction products. In the reaction of phthalodinitrile with *p*-phenylenediamine, it was established at various stages of the latter that, when the reaction is carried out in solvents other than phenols with electron-accepting substituents, the intermediates contain compounds with m/z = 236, 327, and 455.

The following expanded mechanism of the reaction of phthalodinitrile with *p*-phenylenediamine in phenol, where the macroheterocycle was obtained in maximum yield, was proposed on the basis of these data (Scheme 3).

The results presented permit the fundamentally important conclusion that one of the decisive factors determining the composition of the products of the condensation of phthalodinitrile with aromatic diamines in hydroxylated solvents is the nature of the reaction medium. Since the condensation of phthalodinitrile with diamines in phenol is the most selective process in the formation of hexazocyclanes, the kinetics and mechanism of this reaction were investigated in detail.

The thermodynamics of the process were investigated for the condensation of phthalodinitrile with *m*-phenylenediamine.[27] Table 1 presents the enthalpies, entropies, and Gibbs free energies as well as equilibrium constants for this reaction at different temperatures. The negative Gibbs free energies indicate that the synthesis of the hexazocyclane is thermodynamically

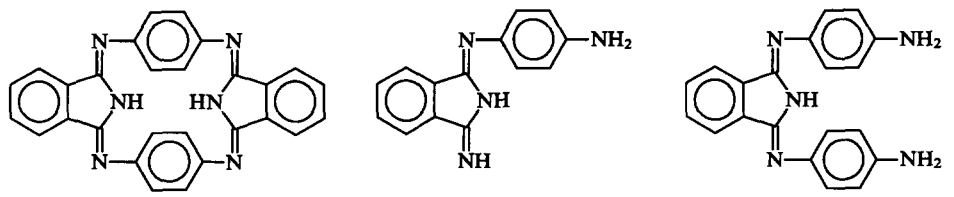
Scheme 1



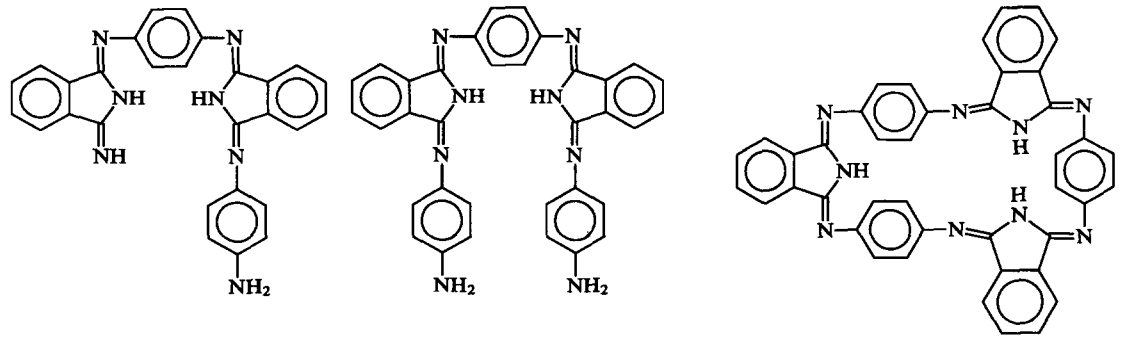
X = Cl, m/z = 347;
X = NO_2, m/z = 358;

X = Cl, m/z = 586;
X = NO_2, m/z = 597.

Scheme 2

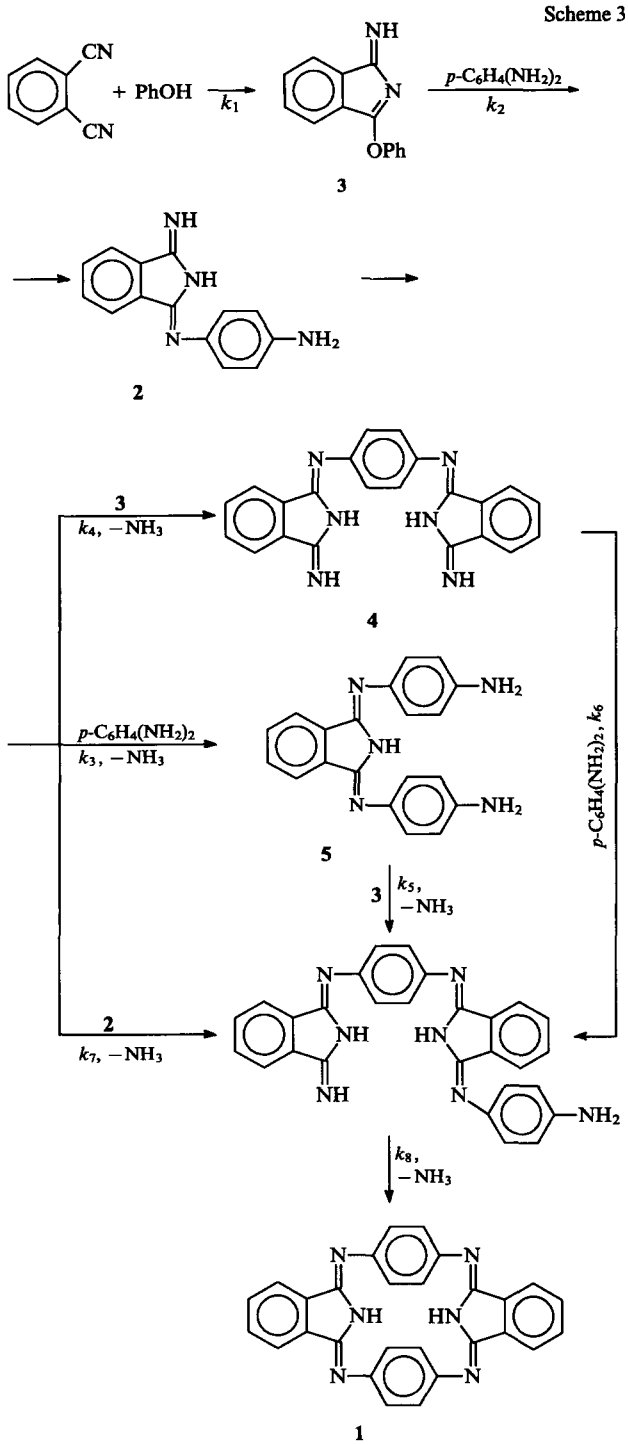


m/z = 438 m/z = 236 m/z = 327



m/z = 455 m/z = 546 m/z = 657

Scheme 3



allowed throughout the temperature range investigated. The equilibrium constant of the reaction is $9.3 \times 10^5 - 5.3 \times 10^3$, so that the condensations of phthalodinitrile with diamines are irreversible. In the temperature range 420–500 K, the entropy of reaction is negative. The high negative enthalpy of the process is responsible for its being thermodynamically allowed and for its irreversibilty.

Since the formation of the hexazocyclane is a multistage process, its overall irreversibility does not rule out the reversibility of individual stages. The study of the composition of the products of the reaction of the hexazocyclane with ammonia — a low-molecular-mass product of this reaction — under the conditions of the synthesis[28] made it possible to put forward Scheme 4 for the ammonolysis of the hexazocyclane.

Table 1. The enthalpies, entropies, Gibbs free energies, and equilibrium constants for the condensation of the dinitrile of *o*-phthalic acid (DN) with *m*-phenylenediamine (*m*-PDA) (p = 101.325 kPa).

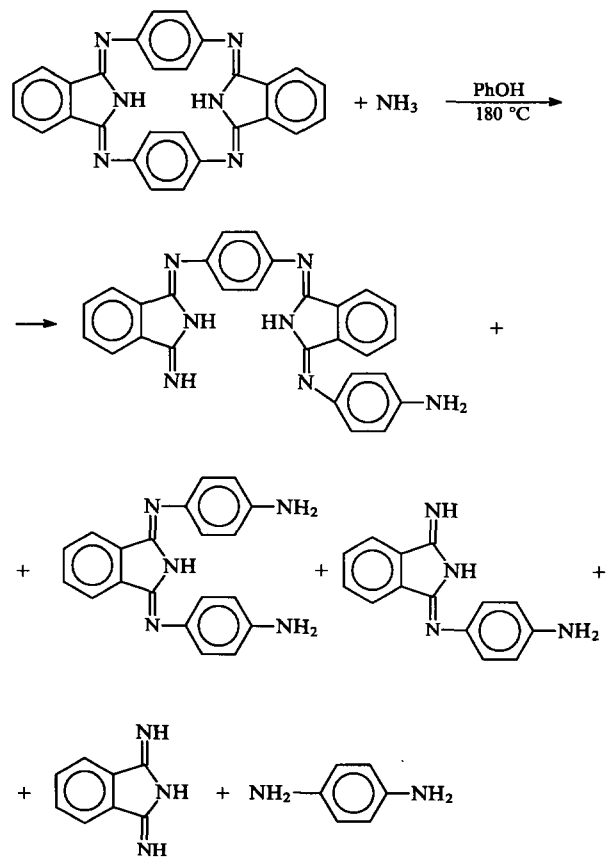
T/K	$-\Delta H_r^\circ(T)$/ kJ mol^{-1}	$-\Delta S_r^\circ(T)$/ J mol^{-1} K^{-1}	$-\Delta G_r^\circ(T)$/ kJ mol^{-1}	lgK_e
2DN(c) + 2*m*-PDA(c) → HC(c) + 2NH$_3$(g)				
250	5.88	−134.6	39.53	8.258
298.15	11.38	−115.8	45.83	8.027
2DN(c) + 2*m*-PDA(l) → HC(c) + 2NH$_3$(g)				
350	50.74	1.92	50.07	7.472
400	62.40	32.35	49.46	6.456
2DN(l) + 2*m*-PDA(l) → HC(c) + 2NH$_3$(g)				
420	106.4	139.2	48.00	5.969
440	110.4	148.4	45.06	5.349
460	114.1	156.7	42.01	4.770
480	117.7	164.1	38.87	4.229
500	121.1	170.9	35.66	3.725

Note. The following notation has been adopted: c = crystal, l = liquid, g = gas, HC = hexazocyclane.

Comparison of the reactions involving the synthesis and ammonolysis of the hexazocyclane provided grounds for the hypothesis that the stages in its formation which take place with evolution of ammonia are reversible, i.e. that the process irreversibility should be attributed to its initial stages.

The kinetics and mechanism of the formation of the hexazocyclane were investigated for the reaction of phthalodinitrile with *p*-phenylenediamine. The process was followed from the decrease in intensity of the C≡N absorption band of phthalodinitrile in the IR spectrum of the reaction solution and

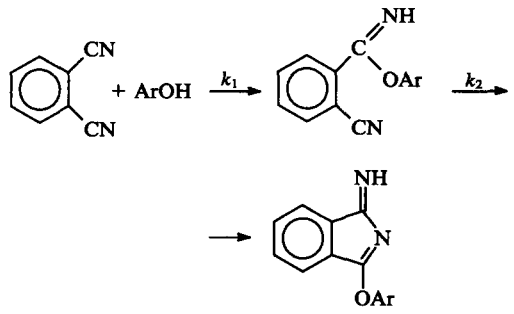
Scheme 4



from the evolution of ammonia. In order to determine the contribution of the individual stages to the formation of the macroheterocycle and to establish the most probable mechanism, mathematical modelling was used with preliminary estimation of the rate constants for those stages where it was possible.

In terms of Scheme 3, the first stage of the reaction is the interaction between phthalodinitrile and phenol. According to literature data,[29,30] there is an excess electron density in the phthalodinitrile molecule on one of the nitrogen atoms and a deficiency on the carbon atoms of the nitrile groups, the positive charge on the carbon atom on one of the nitrile groups being much higher than that on the carbon atom of the other group. This justifies the hypothesis that the reaction begins with nucleophilic attack by the phenol on the carbon atom with the greater positive charge.

The next stage is apparently nucleophilic attack by the nitrogen of the imino-group on the carbon atom of the second nitrile group with subsequent isomerisation and cyclisation.

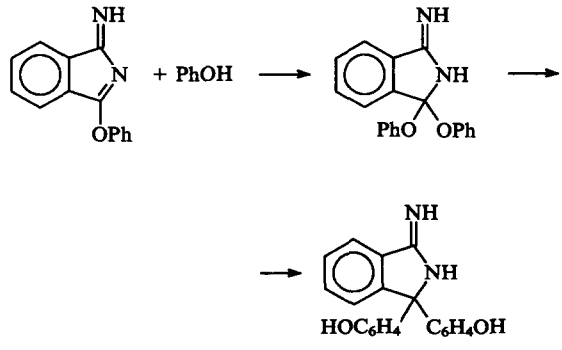


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However, it was found that the reaction product is 1-(4-hydroxyphenyl)-1-(2-hydroxyphenyl)-3-iminoisoindoline **7** and not 1-aryloxy-3-iminoisoindole **6**.[31] This gives grounds for the assumption that the 3-imino-1-phenoxyisoindole formed is an unstable compound, which, having combined with a phenol molecule, undergoes a rearrangement, which is consistent with the hypothesis put forward by Bartlett.[32]

Judging from the fact that there is no compound **7** among the products of the reaction of phthalodinitrile with diamines in phenol, the rate of reaction of the aryloxy-group with the amino-group is higher than the rate of its reaction with phenol.

Taking into account the proposed mechanism for the additional polarisation of the nitrile groups, it was decided to employ LiCl as the catalyst (the polarising effect of the Li^+ ion amounts to 1.7).[33]



7

Studies of the kinetics of the interaction of phthalodinitrile with phenol have shown[34] that there is an induction period in the reaction, which becomes shorter after the introduction of LiCl. The fact that the rate of reaction increases as a function of time is extremely important. This justifies the hypothesis that the process is autocatalytic.

Indeed, it was found that, when 1-(4-hydroxyphenyl)-1-(2-hydroxyphenyl)-3-iminoisoindoline is introduced into the reaction mixture, the induction period is markedly shortened. This is apparently associated with the presence in compound **7** of a secondary cyclic amino-group, the interaction of which with the phenolic hydroxyl increases the electron density on the oxygen atom, thereby increasing the rate of the reaction of phenol with the electrophilic carbon atom.

Other cyclic amines exhibit in this reaction a catalytic activity,[34] which increases with increase in the basicity of the amine. When a tertiary amine and LiCl are introduced simultaneously into the reaction, both reagents are activated and the induction period virtually vanishes.

The following reaction rate constants have been obtained from kinetic data with the aid of the mathematical model:

$$k_1/h^{-1} = 0.004 + 1.6\,c_{LiCl} + 7\,c_7,$$

$$k_2/h^{-1} = 5.$$

The results show that both LiCl and compound **7** are catalysts of the first stage of the reaction, the catalytic activity of the latter being higher. The cyclisation stage is noncatalytic. The proposed mechanism of the reaction of phthalodinitrile with phenol is confirmed indirectly by the shortening of the induction period with increase in the nucleophilicity of phenols caused by the introduction of electron-donating substituents into the benzene ring.

The product of the reaction of a substituted phthalodinitrile containing an electron-accepting substituent with phenol is 3-imino-1-phenoxyisoindole. The latter compound does not combine with a second phenol molecule and does not rearrange. Kinetic studies have shown[34] that the rate of reaction of phenol with substituted phthalodinitriles depends on the nature of the substituent in the phthalodinitrile and increases as its electron-accepting properties become more pronounced. The equations for the rate constants for the reaction of 4-nitrophthalodinitrile with phenol have the following form:

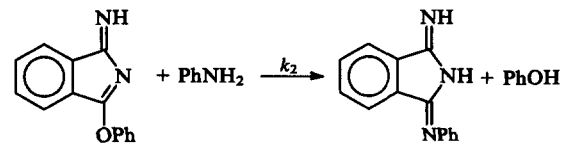
$$k_1/h^{-1} = 0.075 + 25\,c_{LiCl} + 11\,c_7,$$

$$k_2/h^{-1} = 9.$$

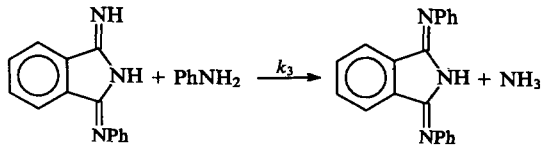
From the above equation for k_1, when the nitro-group is introduced into the phthalodinitrile ring, the contribution of the catalytic reaction increases appreciably (compared with the unsubstituted phthalodinitrile). This is accompanied by a sharp increase also in the catalytic activity of LiCl. Evidently, the increase in the positive charge on the carbon atoms of the nitrile groups facilitates their nucleophilic attack by phenol in the first stage of the reaction by the nitrogen of the free C≡N group in the second stage.

When the electron-donating OH group is introduced into the ring of phthalodinitrile, a sharp decrease in the reaction rate is observed, which is fully consistent with the proposed mechanism.

The next stage of macroheterocycle formation, the interaction of 3-imino-1-phenoxyisoindole with the diamine, was investigated for the reaction of phthalodinitrile with aniline at 20–180 °C in view of the complexity of the process.[35] It was found that, at temperatures below 70 °C, 3-imino-1-phenoxyisoindole interacts with aniline via the phenoxy-group.

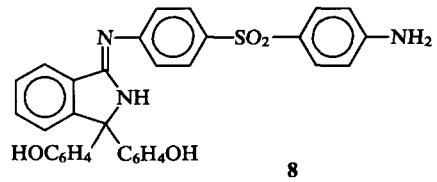


At a temperature above 70 °C, aniline behaves as a nucleophilic relative to the carbon atom of the C≡N group. The reaction of aniline with 1,3-diiminoisoindole results in the evolution of ammonia, which is apparently formed by the addition of the aniline protons to the exocyclic NH group.[36]

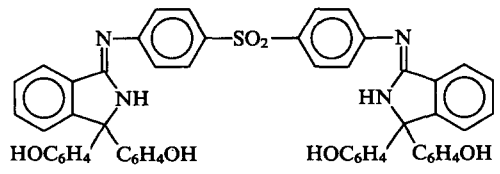


Calculation of the reaction rates by means of the mathematical model for the process showed[37] that the rate of reaction of phthalodinitrile with phenol diminishes sharply in the presence of aniline. Comparison of the equations for the rate constants showed that aniline appreciably lowers the catalytic activity of LiCl, apparently due to the formation of the complex $LiCl-PhNH_2$. The rate-limiting stage of the process is the formation of this complex.

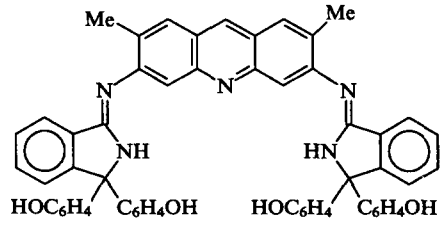
Since the condensation of the amino-group with the phenoxy- and imino-groups takes place via a nucleophilic substitution mechanism, the basicity of the amine should influence significantly the rate and mode of the reactions. The study of the composition of the products of the reaction of phthalodinitrile with 3,6-diamino-2,7-dimethylacridine ($pK_a = 1.5$), di(4,4-aminophenyl) sulfone ($pK_a = 2.7$), 9,9-bis(4-aminophenyl)-fluorene ($pK_a = 3.3$), and *p*-phenylenediamine ($pK_a = 6.2$) in phenol showed that, instead of the macroheterocycles, the corresponding compounds **8–11** are formed in the first two cases.



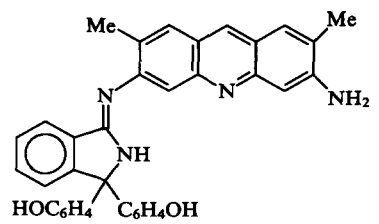
8



9

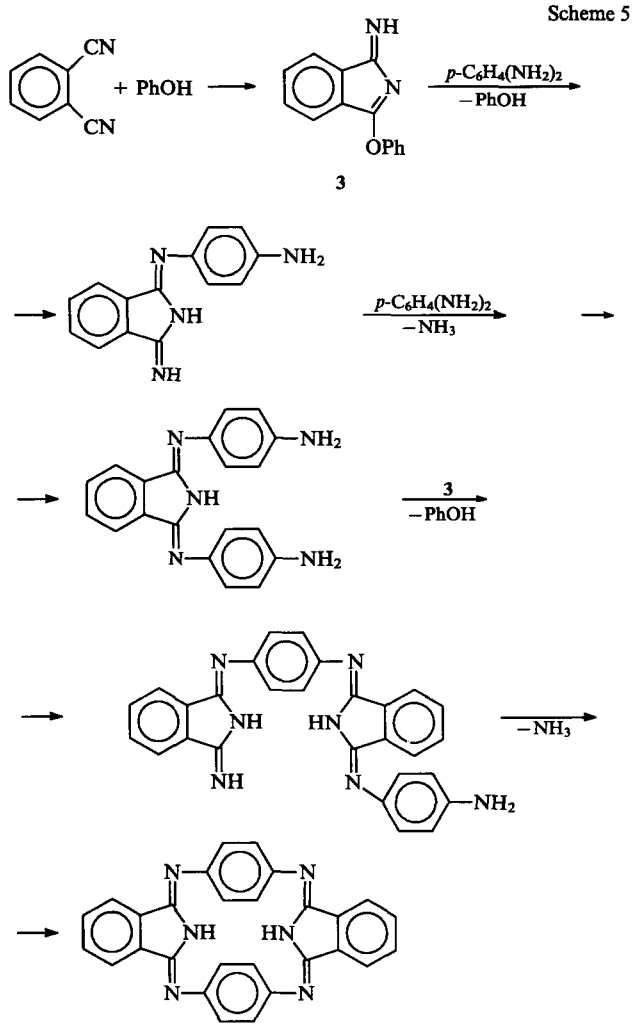


10, $m/z = 835$

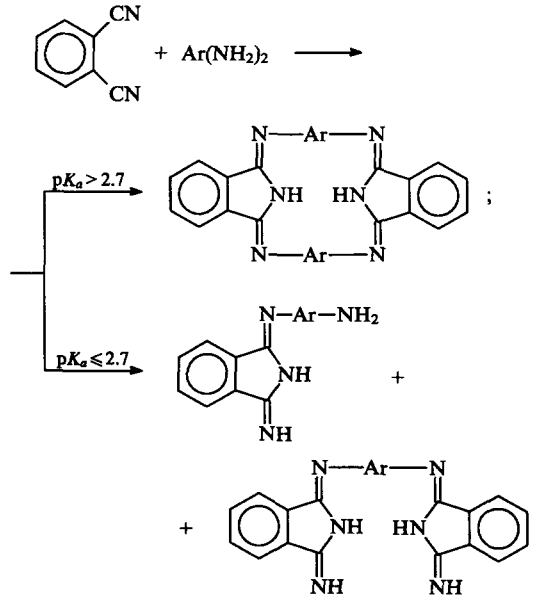


11, $m/z = 537$

Scheme 5



Apparently, owing to the low basicity of these diamines, the rate of reaction of the amino-groups with the phenoxy-group in compound **3** (see Scheme 3) is lower than the rate of formation of compound **2**, which actually reacts with the diamine. In all the remaining cases, macroheterocycles are formed. From these data, the interaction of phthalodinitrile with diamines can be represented by the following general scheme as a function of the basicity of the diamines:



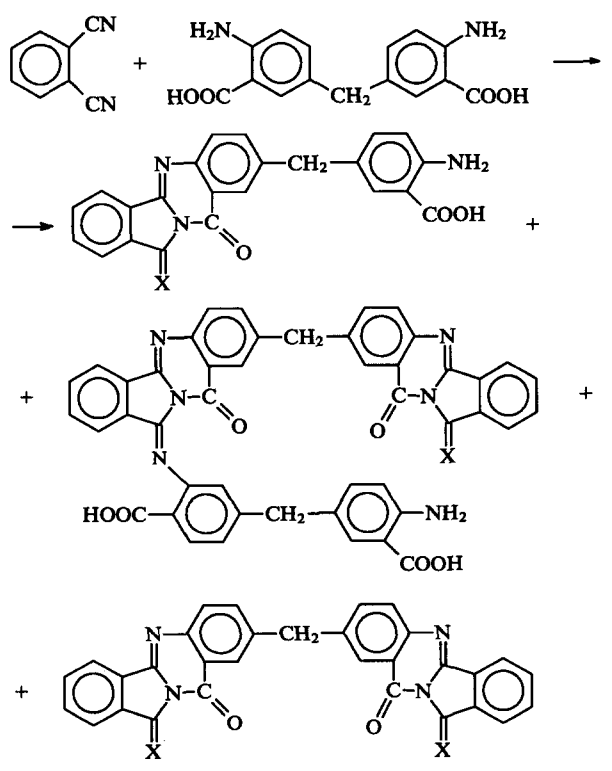
The kinetics of the formation of the macroheterocycle have been investigated for the condensation of phthalodinitrile with *p*-phenylenediamine.[40] The mathematical description of the process made it possible to calculate the rates of all the reactions constituting the formation reaction of the hexazocyclane and to determine its principal aspects (Scheme 5, see previous page).

Direct experimental confirmation of the macrocyclic structure of the hexazocyclane was obtained by X-ray diffraction study of the hexazocyclane based on phthalodinitrile and di(4,4-aminophenyl) ether.[31] The geometry of the principal groups of atoms is close to the usual geometry, i.e. the formation of the macroheterocycle hardly requires the distortion of the bond angles and bond lengths. The conformation of the five-membered nitrogen-containing heterocycles is nearly planar (the endocyclic torsional angles do not exceed 4.4°). However, in combination with some twisting about the endocyclic C–N bonds, this proves sufficient for a significant deviation of the conformation of the macrocycle itself from planarity.

Hexazocyclanes contain water in the endocyclic space, i.e. they are clathrate compounds. In contrast to the majority of known clathrate compounds, for hexazocyclanes the guest molecule inclusion cage consists of a single molecule; hexazocyclanes based on mononuclear diamines contain one water molecule in the endocyclic space, whilst the remaining hexazocyclanes contain two such molecules regardless of the size of the macroheterocycle.[41]

III. Macroheterocycles with a system of five- or six-membered heterocycles condensed with the isoindole ring

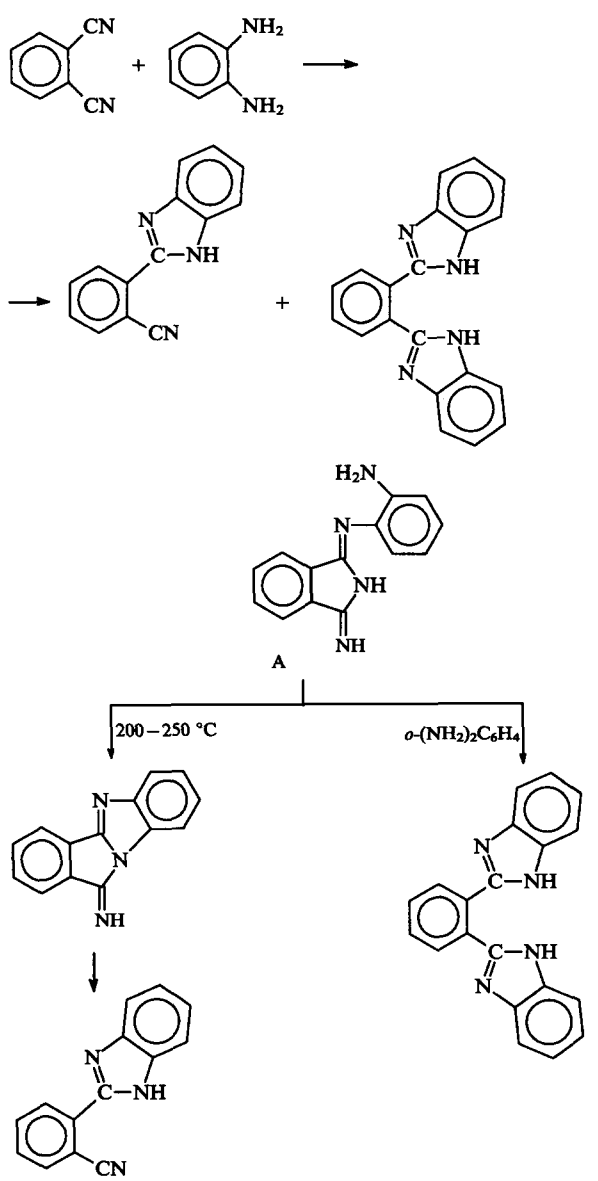
Macroheterocycles with a system of condensed heterocycles can be formed if a diamine, containing *ortho*-substituents capable of interacting with the secondary amino-groups of the isoindole ring, is used as one of the initial reactants. Such reactions proceed both with the evolution of volatile products and via isomerisation cyclisation. This requires a high reactivity of the *ortho*-substituents. For example, they may contain a labile hydrogen atom, the interaction of which with the NH group of the isoindole ring is accompanied by water or ammonia evolution.



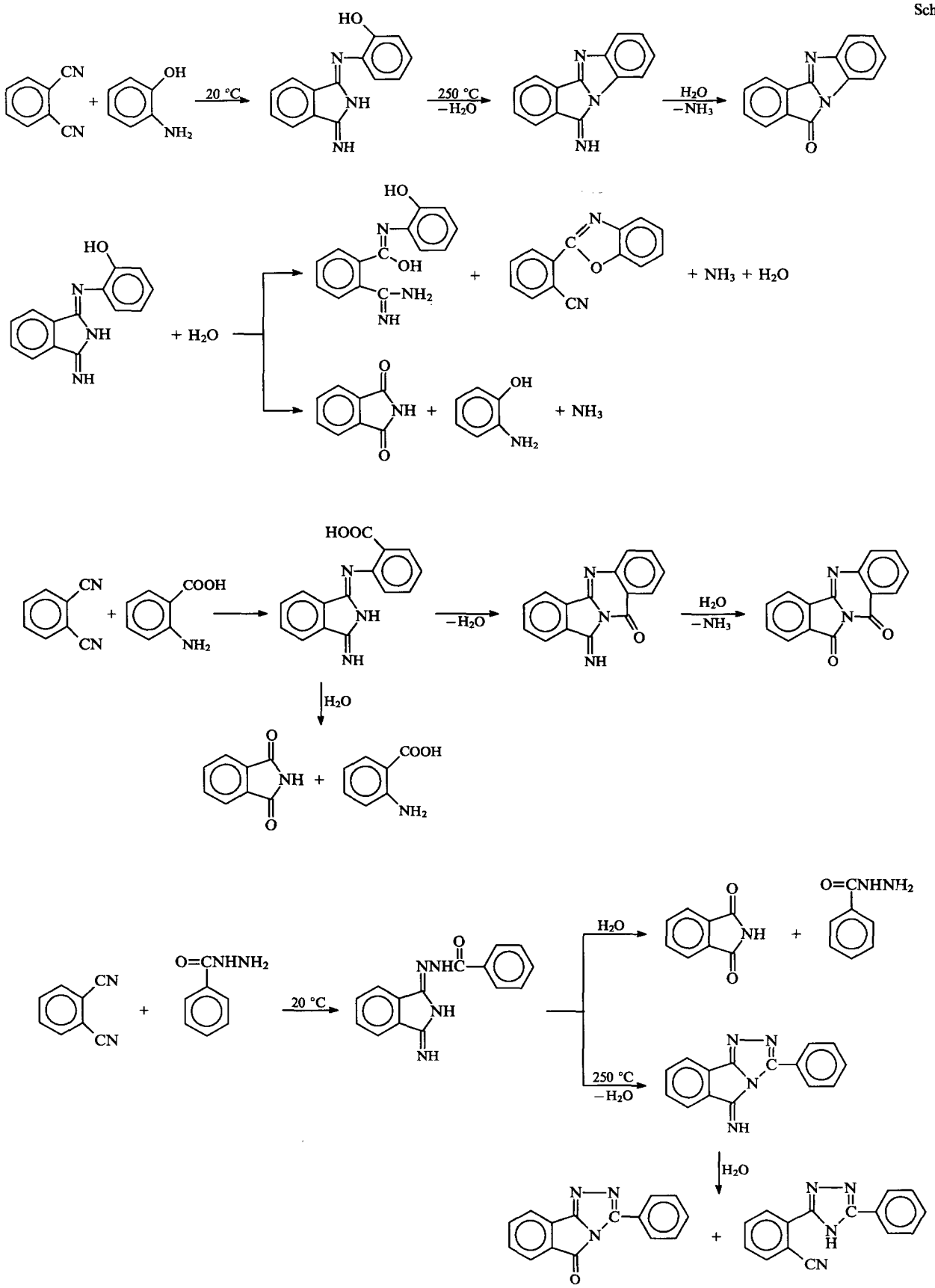
X = O, NH

The mechanism of this process has been studied for the condensation of phthalodinitrile with *ortho*-substituted monoamines—*o*-aminophenol, anthranilic acid, and benzohydrazide.[42] When these diamines interact with the imino-group of the isoindole ring, water is liberated. The thermal cyclisation process was investigated using compounds obtained by condensing phthalodinitrile with a monoamine at room temperature. At 200–250 °C both the formation of compounds with condensed heterocycles and the hydrolysis of the final and intermediate products take place (Scheme 6). Therefore, the possibility of using polyphosphoric acid (PPA) as the reaction medium, which binds the water evolved on cyclisation, was investigated in the condensation of phthalodinitrile with anthranilic acid. The composition and structure of the products of this reaction were found to be determined by the temperature and the order in which the reactants are added. The selectivity of the reaction of phthalodinitrile with anthranilic acid is ensured by introducing the acid at $T > 180$ °C into a solution of phthalodinitrile.

However, the reaction of phthalodinitrile with methylenedianthranilic acid proceeds under these conditions without the formation of a macroheterocycle.[43] (See bottom left.)



Scheme 6

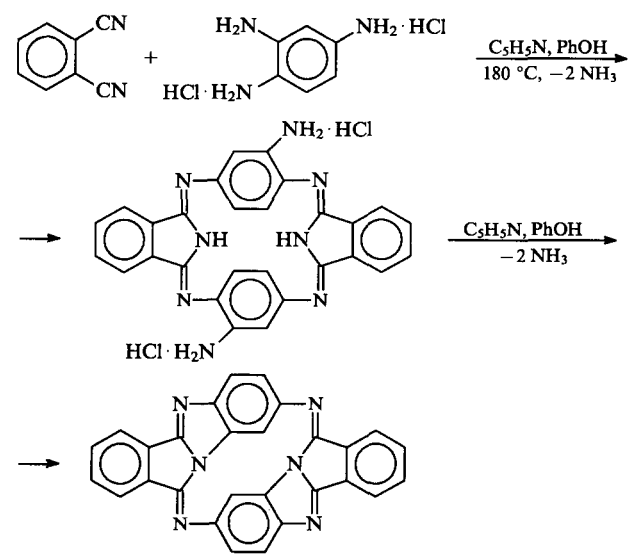


The fact that, instead of the macroheterocycle, only the intermediates in its synthesis are formed in the condensation of phthalodinitrile and *p*-phenylenediamine in PPA is extremely important. The same products, isolated from PPA and then placed in phenol, interact with the latter, affording a hexazocyclane. In the condensation of phthalodinitrile with 1,2,4-triaminobenzene, the formation of a system of condensed isoindole and benzimidazole rings should be accompanied by ammonia evolution. To find out whether such a reaction occurred, a comparison was made of the product composition of the condensation of *o*-phenylenediamine with phthalodinitrile in phenol at 180 °C [44] and of the cyclisation products of 1-*N*-(2-aminophenyl)-3-iminoisoindoline at 200–250 °C in the presence and absence of *o*-phenylenediamine (see page 772, bottom right).

It follows from a comparison of the results that the factors preventing the formation of compounds with a system of condensed isoindole and benzimidazole rings are the isomerisation of compound **A** with participation of the exocyclic NH group during the cyclisation process as well as the interaction of the intermediate — 1-*N*-(2-aminophenyl)-3-iminoisoindoline — with *o*-phenylenediamine. This required as the initial reactant not *o*-phenylenediamine itself but a derivative with a substituted amino-group. Furthermore, it is necessary that substitution of the exocyclic NH groups should precede formation of the benzimidazole ring.

Therefore, 1,2,4-triaminobenzene in the form of the 1,4-dihydrochloride was used as the amine component for the synthesis of a hexazocyclane with condensed benzimidazole and isoindole rings. During the synthesis, the hydrochloride groups were neutralised in two stages. Judging from literature data,[44] the 4-amino-group is the first to be neutralised, which is the reason for the possibility of macroheterocycle formation. After the neutralisation of the second amino-group, the latter reacts quantitatively with the NH group of the isoindole ring to form condensed heterocycles.[45] (See above right.)

In order to obtain compounds with a system of condensed heterocycles without the isolation of volatile products, the dinitrile of methylenedianthranilic acid was used as the amine component in the reaction with phthalodinitrile in phenol, because in this case the quinazoline ring is formed via isomerisation cyclisation.[46] A quantitative estimate by IR showed that the hexazocyclane

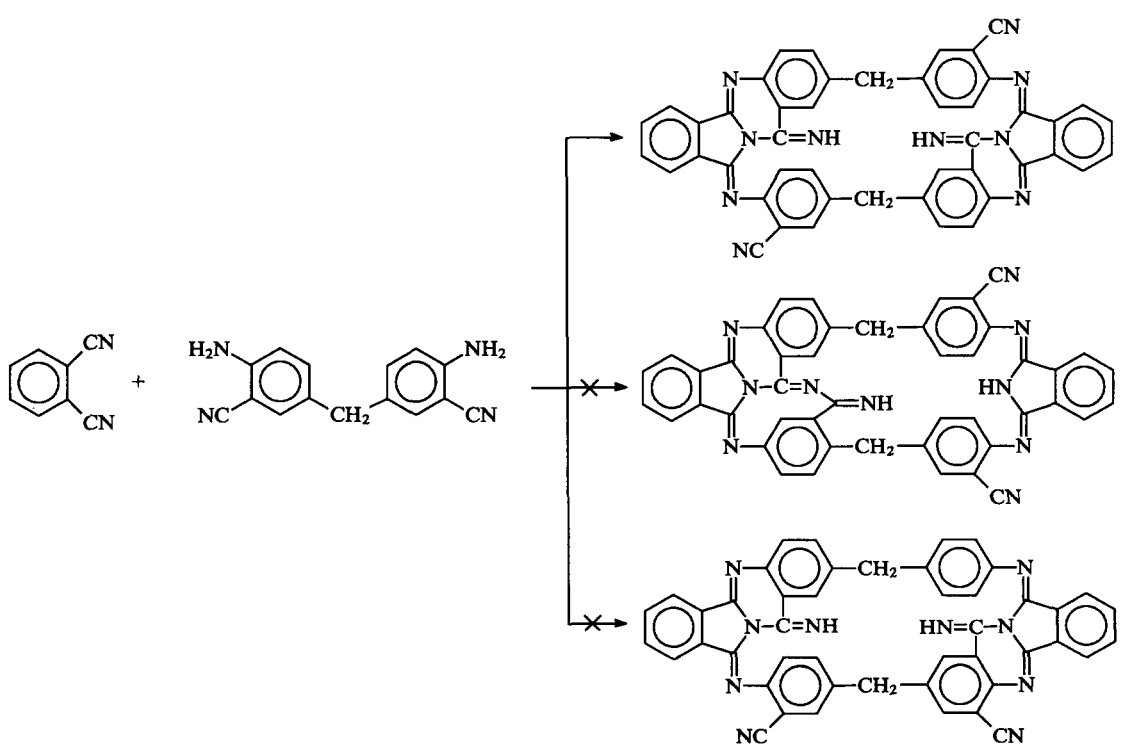


contained two free C≡N groups, which justifies the hypothesis that three isomers of the macroheterocycle differing in the position of the C≡N groups are formed. Studies showed that the reaction proceeds strictly selectively only via a single pathway with formation of a macroheterocycle having the structure presented in Scheme 7.

The selectivity of the reaction is evident because, as a result of the interaction of one of the nitrile groups with the imino-group of the isoindoline ring, the benzene ring incorporating this nitrile group rotates until it coincides with the average plane of the macroheterocycle. The plane of the second benzene ring should then be inclined relative to the average plane of the macroheterocycle. The distance between the nitrile group of this ring and the imino-group of the isoindole ring increases, which rules out the possibility of intramolecular cyclisation.

The data obtained in the study of model reactions of phthalodinitriles with diamines served as a basis for the development of specific methods of synthesis, from tetracarboxylic acid tetranitriles and diamines, of polymers both having a macrocyclic structure and without macroheterocycles.

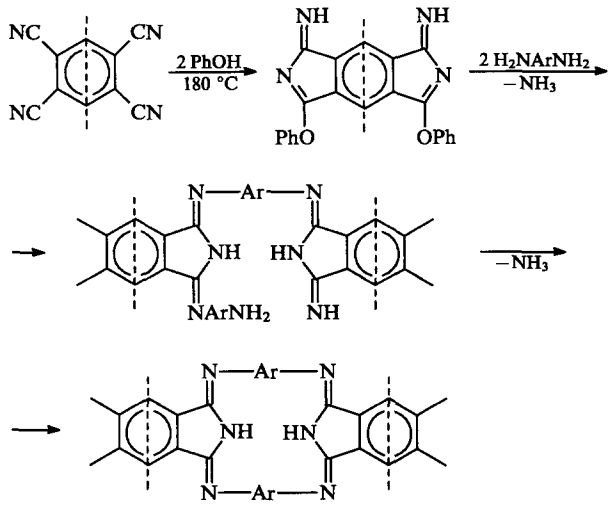
Scheme 7



IV. Polycondensation of tetracarboxylic acid tetranitriles and unsubstituted diamines in phenol

The data obtained in the study of model reactions of phthalodinitriles with diamines give grounds for the assumption that polymers with the maximum content of macroheterocycles in the chain can be obtained by the polycondensation of tetracarboxylic acid tetranitriles and highly basic ($pK_a > 3.3$) aromatic diamines in phenols ($pK_a > 9.8$). The polycondensation process can be represented by the multistage Scheme 8.

Scheme 8



The polymer chain grows by accumulation in the latter of macroheterocycles, the formation of which is accompanied by ammonia evolution. Hence, the amount of ammonia evolved is used as a measure of the degree of reaction and of the propagation of the polymer chain. The structure of the polymers has been confirmed by ^1H NMR spectroscopic data[26] obtained in the study of a polyhexazocyclane (PHC) based on pyromellitic acid tetranitrile and *p*-phenylenediamine.

Kinetic studies of the reaction of tetracarboxylic acid tetranitriles and diamines show that the polycondensation process is autocatalytic. By analogy with the model reaction, one can postulate that the autocatalysts of the polycondensation process are intermediates containing a cyclic imino-group. The use as the catalyst of a tertiary cyclic amine with LiCl leads to the disappearance of the induction period and to an increase in reaction rate.

The set of monomers which has been used to synthesise PHC made it possible to trace in succession the influence of their structure on the properties of the polymers.

It follows from Table 2 that a high degree of reaction and a high yield are characteristic of all the PHC. The solubility of the polymers is determined by their structure. The introduction into the monomer of a cardo-group and of an oxygen bridge between the benzene rings increases the range of solvents in which the PHC dissolve.[21]

All the PHC possess a high thermal stability and heat resistance. According to dynamic thermogravimetric analyses (TGA), the temperature of the onset of their vigorous decomposition in air exceeds 400 °C. A more complete idea about the thermal transformations of PHC has been obtained in the study of the composition of the products of the thermal and thermohydrolytic degradation of the macrocycle based on phthalodinitrile and *p*-phenylenediamine as well as a series of PHC at 350–600 °C.[47]

The presence in the thermal degradation products of the macrocycle of carbon oxides, ammonia, phthalimide, and *p*-phenylenediamine suggested that carbon oxides [carbon dioxide only? (Ed. of Translation)] are formed as a result of the hydrolytic cleavage of the hexazocyclane (Scheme 9).

The main hydrolysing agent is apparently the water enclosed in the macroheterocycle. This hypothesis is supported by the finding that the products of degradation (at 400–450 °C) of a hexazocyclane, the endocyclic space within which was occupied by other groups[41] or of a hexazocyclane from which the occluded water had been removed by sublimation, contained only traces of CO_2.

The overall data obtained in the study of the degradation products justified the hypothesis that hydrolytic decomposition processes dominate in the thermal degradation of hexazocyclanes and polymers up to 450 °C, while above 450 °C homolytic decomposition processes assume this role, as indicated by the appearance of hydrogen, methane, and carbon monoxide in the decomposition products.

One of the real routes to increasing the thermal stability of the PHC involves the synthesis of polymers the endocyclic part of the space within which is occupied by groups of some kind, which rules out the presence of occluded water. The preparation of polymers containing five- or six-membered heterocycles condensed with the isoindole ring is most promising in this respect.

Scheme 9

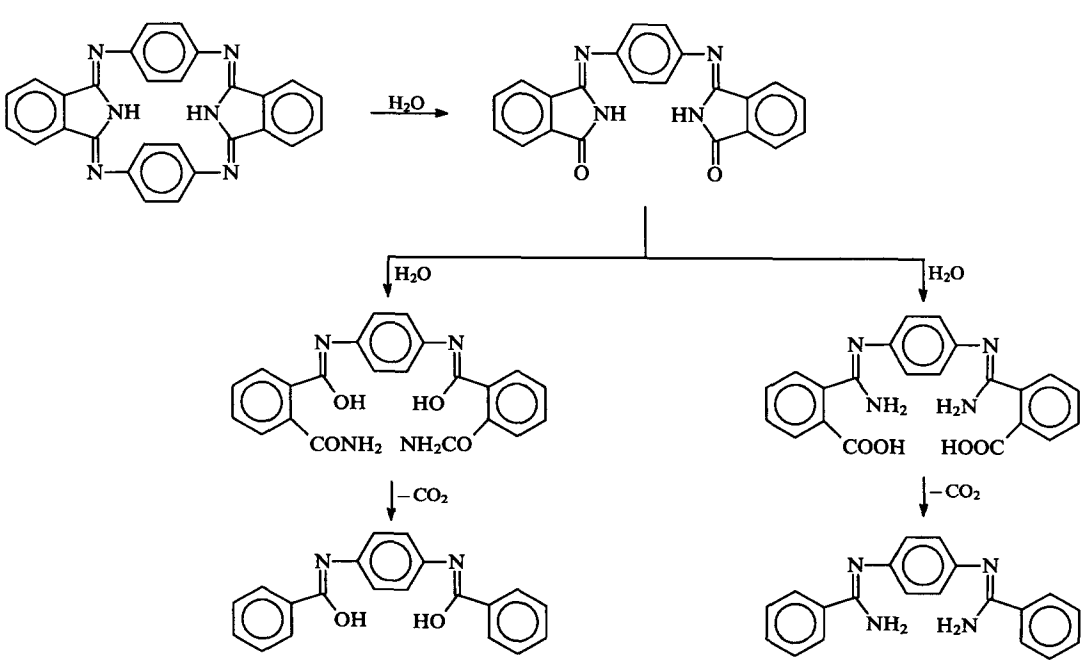
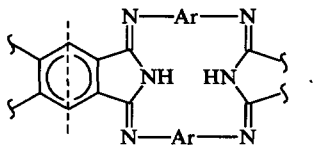
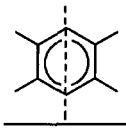
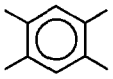
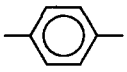
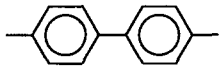
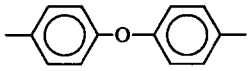
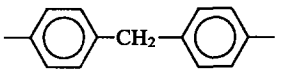
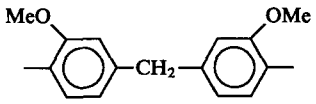
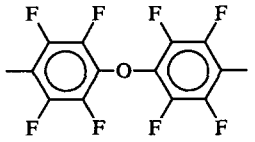
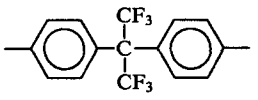
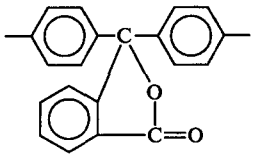
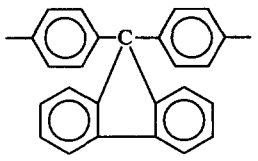
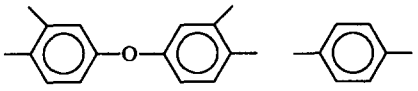


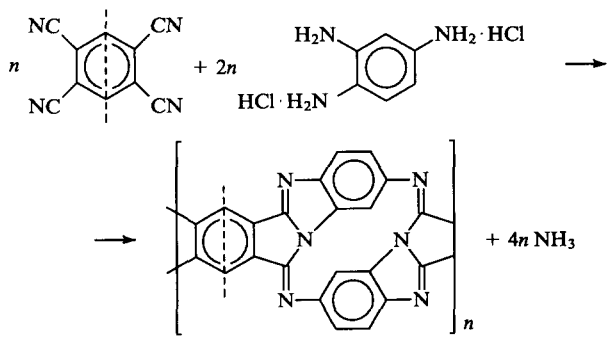
Table 2. The properties of polyhexazocyclanes having the general formula



	—Ar—	Degree of reaction (%)	Yield of polymer (%)	Solvents [a] in which polymers dissolve	Temperature of onset of softening [b]/°C	Temperature of onset of decrease in mass [c] in air/°C
		98	99	H_2SO_4	Does not soften	400
		98	99	H_2SO_4	"	420
		95	95	DMF, HMPA, DMSO, *N*-MP	225	400
		98	99	H_2SO_4	370	410
		97	98	DMF, HMPA, DMSO, *N*-MP	180	350
		91	95	DMF, DMA, *N*-MP, DMSO, acetone, dioxane	210	410
		95	95	"	180	380
		98	97	DMF, HMPA, DMSO, *N*-MP	380	410
		99	98	DMF, DMSO, *N*-MP, dioxane	220 (p = 19.6 MPa)	430
		97	92	DMF, DMSO, *N*-MP, HMPA	180	410

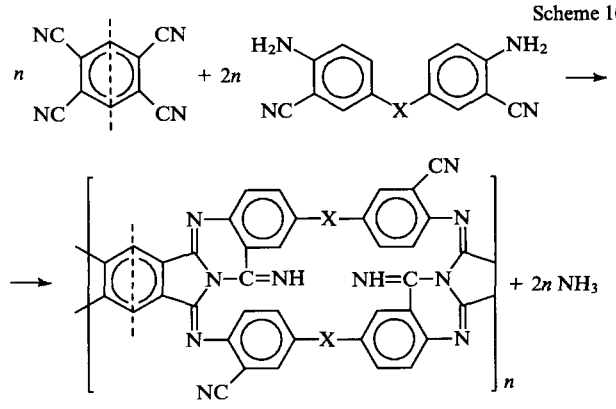
[a] DMF = dimethylformamide, HMPA = hexamethylphosphoramide, DMSO = dimethyl sulfoxide, *N*-MP = *N*-methylpyrrolidinone [DMA = dimethylacetamide (Ed. of Translation)].
[b] Rate of temperature rise 10 °C min^{-1}, p = 9.8 MPa.
[c] Rate of temperature rise 4.5 °C min^{-1}.

Polyhexazocyclanes with condensed isoindole and benzimidazole rings have been obtained by polycondensation of tetracarboxylic acid tetranitriles and diamine dihydrochlorides,[48] the latter being neutralised during the synthetic process.



Polyhexazocyclanes with condensed isoindole and quinazoline rings have been synthesised using bis(*o*-cyanoarylamines) (Scheme 10).[48]

Scheme 10



The thermal stability of such polymers is much higher than that of the usual polyhexazocyclanes.[49] Hydrolytic processes in polymers with condensed heterocycles are extremely slight. The amount of CO_2 evolved during their thermal degradation is smaller by a factor of 4–6 at 450 °C and by a factor of 2–4 at 500–550 °C than in the degradation of the PHC based on *p*-phenylenediamine. In this case, the hydrolysing agent is apparently adsorbed water, the content of which in the polymers, determined by the Fischer method, does not exceed 1%.

V. The properties of solutions of polyhexazocyclanes

The presence of macroheterocycles in the PHC chain determines the specific properties of dilute and concentrated solutions of these polymers.[50] Thus when the degree of reaction is quantitative, the intrinsic viscosity of 0.3%–1.0% solutions of the polymers in *N*-methylpyrrolidinone (*N*-MP) and dimethylformamide (DMF) is low and independent of concentration. Centrifugation results in the complete precipitation of the polymers from the solutions. This provides grounds for the hypothesis that solutions of PHC in aprotic solvents are not true solutions but approach colloidal or are colloidal solutions. This hypothesis has been confirmed by studies of solutions of PHC in *N*-MP by electron microscopy,[51] according to which the polymers in solution exist in the form of aggregates up to 1.5 μm in size, which is evidently associated with a weak polymer–solvent interaction.

In view of the presence in the macroheterocycle of the tertiary amino-group and on the basis of the available data on the solubility of rigid-chain nitrogen-containing polymers,[52,53] it was postulated that the interaction of the polymers with formic acid, which exhibits protogenic properties, is more intense than the interaction with *N*-MP. Indeed, it was found that the absolute intrinsic viscosities of solutions of the polymers in HCOOH are appreciably higher than those of the solutions in *N*-MP. According to electron microscope data, the polymers exist in formic acid in the form of individual 10–20 nm globular particles.

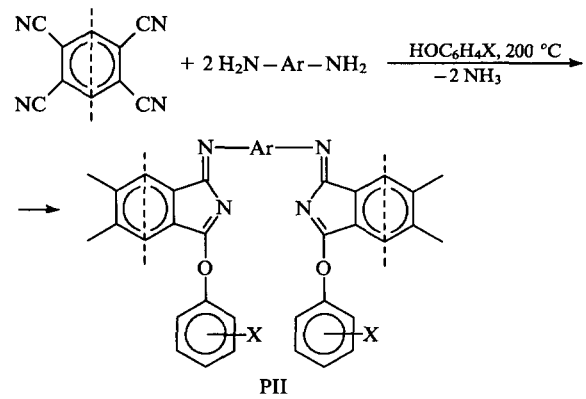
Polymers with charged nitrogen atoms have also been obtained by quaternising them with alkyl halides.[50] The dependence of the viscosity of solutions of such polymers in *N*-MP on the concentration is characteristic of molecularly disperse solutions, while the size of the polymer particles in solution does not exceed 20 nm.

The viscous characteristics of concentrated solutions of PHC are determined by their structure and by the nature of the solvent. Thus, up to a 25%–30% concentration of the PHC in *N*-MP, there is no interaction between the aggregates and the viscosity of the solutions is low and almost independent of concentration. Newtonian flow is characteristic of solutions of PHC in this concentration range. At concentrations above 30% the viscosity rises sharply, evidently at a consequence of the mutual interaction of the aggregates, which leads to a non-Newtonian type of flow.

Starting with a 10% concentration of a solution in formic acid of a rigid-chain polymer, the preparation of which is illustrated in Scheme 10, gel formation takes place which is apparently associated with the mutual arrangement of the extended macromolecules. The modulus of elasticity of a 10% solution of the gel is 6.2×10^{-4} Pa. The high elasticity of the gel is due to the presence in the polymer of nitrile side groups, which are additionally polarised as a result of complex formation with the carboxy-group, intensifying the intermolecular interaction. The modulus of elasticity remains constant up to 70 °C, which distinguishes this gel from the usual heat-treated gels produced as a result of the formation of physical bonds.

VI. Polycondensation of tetracarboxylic acid tetranitriles and diamines in phenols with electron-accepting substituents

Polymers with side aryloxy-groups in the chain, called polyisoindoxazenes (PII) are formed in the polycondensation of tetracarboxylic acid tetranitriles and diamines in phenols with electron-accepting substituents.[54]



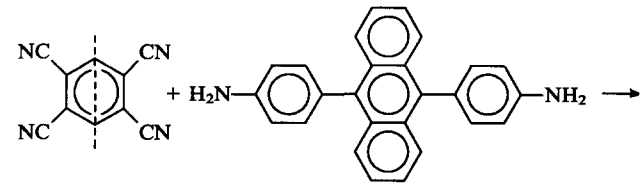
PII

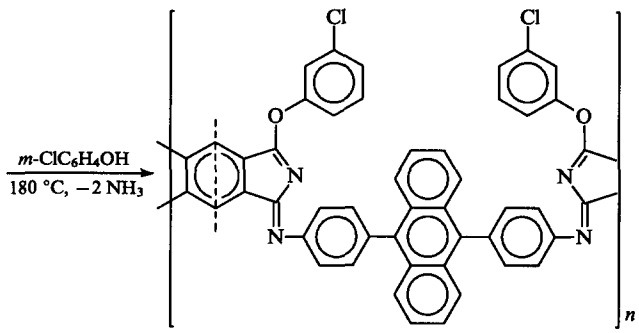
X = Cl, Br, NO_2.

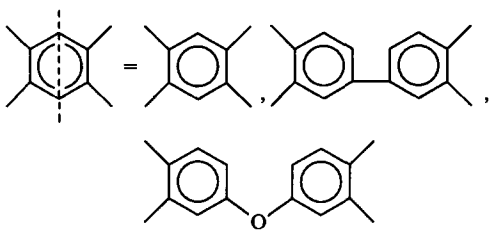
Kinetic studies show that the reaction has an induction period. With increase in the pK_a for a phenol, the duration of the induction period diminishes and the rate of polycondensation rises. From data obtained on model reactions, it is suggested that the process under consideration is autocatalytic, the product of the interaction of the tetranitrile with the phenol playing the role of the autocatalyst. The reaction of the phenol with the *o*-dinitrile is a nucleophilic process, so that the acidity of the phenol determines the rate of formation of the autocatalyst, which is simultaneously a reaction intermediate, and hence the rate of the reaction as a whole.

Polyisoindoxazenes have fairly high thermal stabilities and heat resistances, their thermal stabilities being somewhat inferior to those of the PHC. The temperature corresponding to a 5%

decrease in the mass of these polymers in air does not exceed 400 °C according to dynamic TGA data. As a rule, these polymers are readily soluble in organic solvents. The polymer based on pyromellitonitrile and bis(4,4'-aminophenol)anthracene, which precipitates during synthesis and does not dissolve even in sulfuric acid, is an exception.





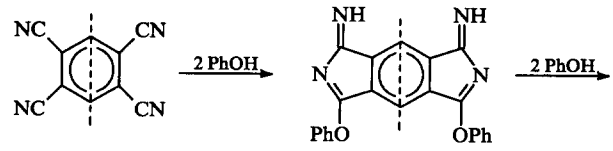


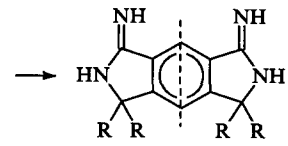
Calculations of the conformational parameters of this PII showed[55] that the rigidity of its macromolecule is such that it cannot form a coil and retains the shape of a straight rigid rod whatever the number of units, which is due to the presence of only a single virtual bond around which rotation is possible. The polymer having this structure has the most rigid chain among all those known at the present time and the concept of the Kuhn segment is not applicable to it. The replacement of pyromellitonitrile by the tetranitrile of oxybis(benzenedicarboxylic) acid results in the appearance in the polymer of additional virtual bonds around which rotation is possible. Under these conditions, the size of the Kuhn segment diminishes to 40 Å and the polymer becomes soluble in organic solvents.

VII. Polycondensation of tetracarboxylic acid tetranitriles and weakly basic diamines

Judging from model reaction studies, in the polycondensation of the tetranitriles and weakly basic ($pK_a < 2.7$) diamines in phenol[56] the first stage in polymer formation is the interaction of the tetranitrile with four phenol molecules and subsequent rearrangement of the phenoxide groups. Compound **12**, formed at this stage, reacts with the diamine.

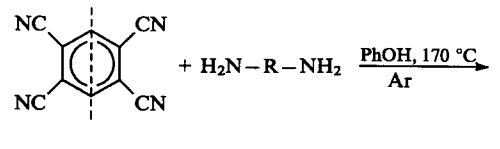
The polymers obtained in this way have been called polyoxyphenylisoindazenes. Their solubilities are higher than those of PHC and PII, whilst their thermal stabilities are comparable with those of the latter compounds. The presence in the polymers of free hydroxy-groups leads to the possibility of extensive modification of their properties by means of further polymer-analogue reactions.

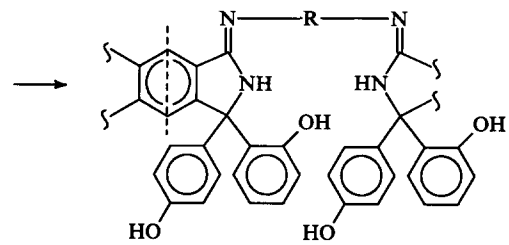


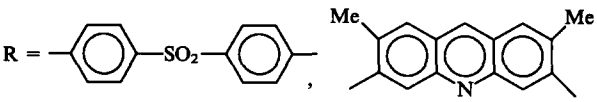


R = C_6H_4OH

12







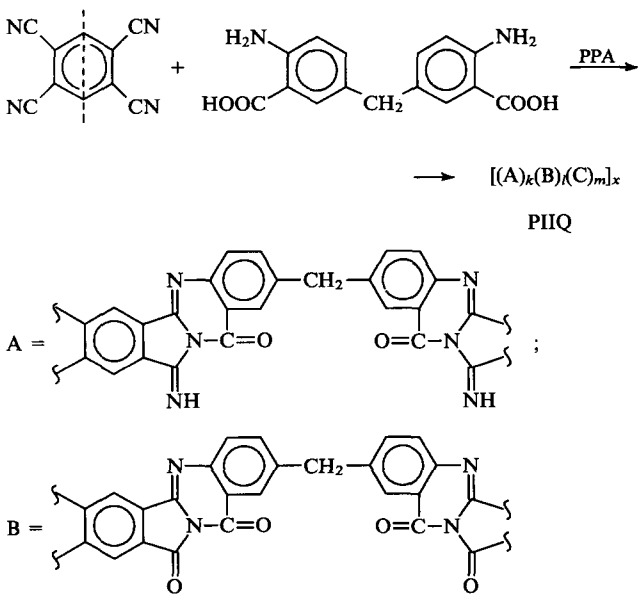
VIII. Polycondensation of tetracarboxylic acid tetranitriles and bisanthranilic acids in polyphosphoric acid

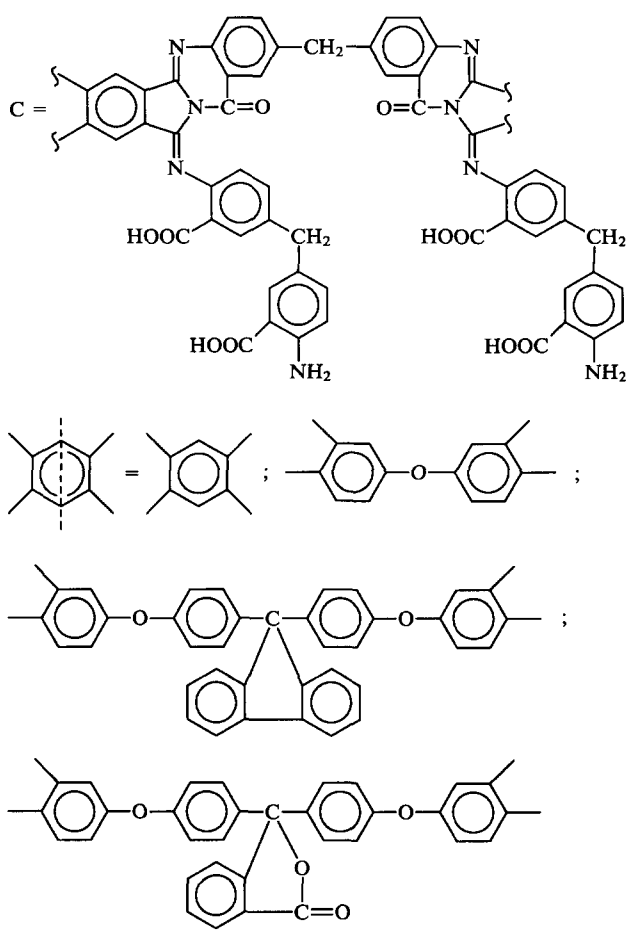
Polymers with a nonmacrocyclic structure, containing condensed isoindole and quinazolinone rings in the chain, have been obtained by the polycondensation of tetracarboxylic acid tetranitriles and bisanthranilic acids in polyphosphoric acid.[42] Such polymers have been called polyisoindolequinazolinones (PIIQ).

Polyisoindolequinazolinonediones, the structure of which is similar to that of the PIIQ, have been obtained by the polycondensation of bis(*o*-aminoamides) [?bis(*o*-aminobenzenecarboxamides) (Ed. of Translation)] with tetracarboxylic acid dianhydrides and also by the interaction of diaminodicarboxylic acids with the dianhydrides and chlorides of tetracarboxylic acid half-esters.[57-61] The possibility of the synthesis of such polymers by polycondensation of derivatives of tetracarboxylic acids with diaminodicarboxylic acids has also been demonstrated.[62,63]

This aspect developed appreciably after the polycondensation of 2,5-dicyanoterephthaloyl chloride with dicarboxy- and bis(methoxycarbonyl)-amines as well as bis(*o*-aminonitriles) had been achieved.[64,65] The use of these compounds made it possible to obtain polyiminoquinazolinepyrrolones via an isomerisation mechanism without the isolation of volatile products.[66]

Polyisoindolequinazolinones are readily soluble in organic solvents and in inorganic acids. Their thermal stability is high: according to dynamic TGA data, the temperature of a 5% decrease in their mass in air is 420–440 °C. Carbon monoxide is completely absent from the products of the degradation of the polymers in vacuo at 400 °C, while at 450 °C its amount is insignificant, which indicates the virtually complete cyclisation of the polymer under the conditions of the synthesis.

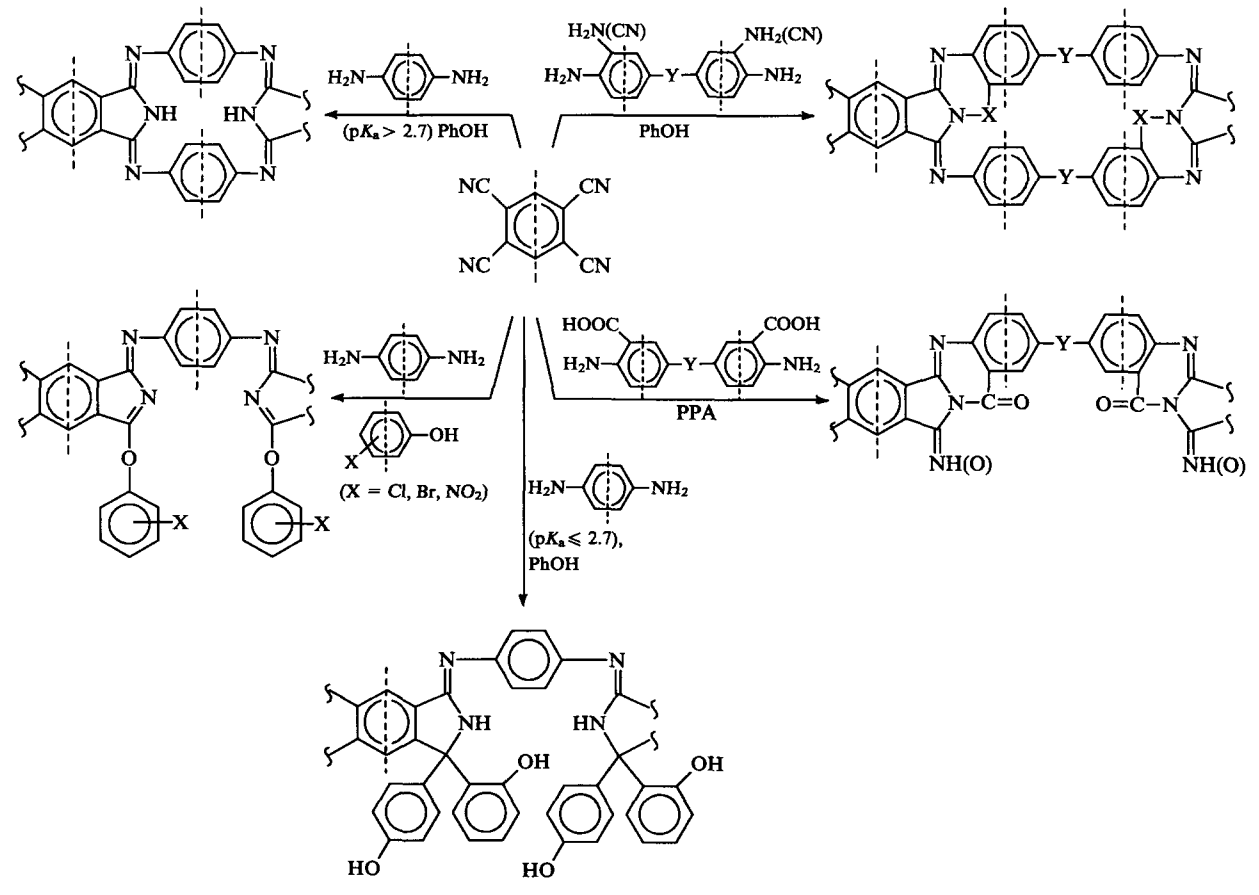




At 500 °C, gas evolution is greater by a factor of 4–5 for polyisoindolequinazolinones than for PHC, indicating an appreciable contribution of the macrocyclic structure to the thermal stability of the polymers (Scheme 11).

Thus the study of the condensation and polycondensation of phthalodinitriles and bis(phthalodinitriles) with diamines demonstrated the extensive synthetic possibilities of these reactions. The determination of the physicochemical characteristics of the processes made it possible to formulate general ideas concerning the mechanisms of these reactions, which provided a basis for the synthesis of a series of new classes of polymers.[6, 7, 21, 42, 43, 48, 67–70]

Scheme 11



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