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PROPERTIES AND APPLICATION OF ARYL-SUBSTITUTED AZINES (Review)

V. P. Borovik and O. P. Shkurko

Aryl-substituted six-membered azaaromatic heterocycles have a range of properties that make it possible to use them in scientific investigations and in modern regions of technology. The possibilities of using arylazines in chemical analysis, in catalytic processes, and as optical and photochromic materials in polymer chemistry are surveyed.

Derivatives of pyridine and di- and triazines containing aryl and heteroaryl groups as substituents exhibit a combination of properties that determine the wide range of their practical applications in scientific investigations, technology, medicine, and agriculture. Interesting properties appear even when phenyl substituents not containing functional groups in the benzene ring are introduced into the azine ring. Thus, 2,3-diphenylpyrazine has a particular smell and taste, making it possible to use it in the food industry as a flavoring additive [1]. Such "aromatic" qualities are also characteristic of other phenylpyrazines with various mutual arrangements of the phenyl and aliphatic substituents in the heterocycle. Their application makes it possible to vary the smell and flavor of food products [2]. They are also used in multicomponent compositions with the mono-, di-, tri-, and tetrasubstituted alkyl and phenyl derivatives of pyrazine in various proportions in the tobacco industry for the treatment of tobacco [3]. Some aryl(heteroaryl)azines are products from natural biogenesis. For example, isomeric phenylpyridines, derivatives of 2-(2-oxazolyl)pyridine, 6-methyl-2-(2-thienyl)pyrazine, 2-(2-furyl)pyrazine and its methyl derivatives, 3-(N-methyl-2-pyrrolyl)pyridine (nicotirine), 2,3′-bipyridine, and 3,2′:4′,3″-terpyridine (nicoteline) were found in various plants and in the products from their treatment [4-12]. The same bipyridine and 3,2:3′,4″:2″,3‴-quaterpyridine (nemerteline) were isolated from marine worms [13, 14]. 4-Methoxy-2,2′-bipyridine 6-aldoxime (kerulomycin A) is a natural antibiotic [15], while the 2-(2-thiazolyl)pyridine fragment enters into the structure of cyclothiazomycin — a polypeptide of microbiological origin [16]. There are data on the presence of compounds with the 2,2′-bipyridine structure in crude oil [17] and of the isomeric bipyridines and their methyl derivatives in tobacco smoke [18].

The introduction of functional groups into the structure of arylazines very often leads to compounds exhibiting biological activity and chelating, mesomorphous, photochromic, and other useful characteristics. The mesomorphous characteristics of such compounds and their use as liquid crystals, which requires special examination, are not discussed in the present review. This applies equally to the biological activity of the functional derivatives of arylazines.

The range of compounds examined in the review is limited to the derivatives of arylazines in which the aryl or heteroaryl groups are directly attached to the azine ring. In addition to such substituents, the heterocycles may also contain various functions, aliphatic radicals, and more complex groups. As a rule, partially or completely hydrogenated azines, their oxo and thio derivatives, N-oxides, and quaternized and condensed heterocycles are excluded.

1. PHOTOCHROMIC AND OPTICAL CHARACTERISTICS OF ARYLAZINES

An important property of aryl-substituted azines, which has found practical application, is the ability to absorb UV rays and transform their energy into soft luminescent radiation. This makes it possible to use such compounds in electroluminescent devices [19]. 2,4,6-Triarylpyridines (I, II) were proposed as light-stabilizing additives for polymeric compositions [20-22].

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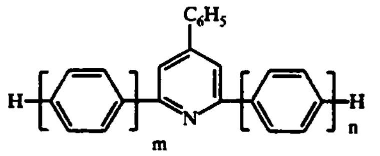
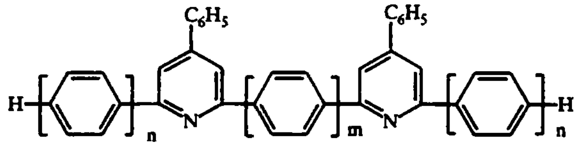


I

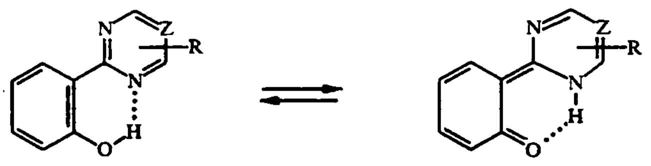


II

m, n = 1, 2, 3

These compounds can also be used as scintillators in counters for the detection and measurement of ionizing radiation [20-22]. It is considered that certain amino derivatives of aryl(heteroaryl)pyrazines, contained in marine plants, in Coelenterata, and in crustaceans, act as emitters for bioluminescence [7].

Aryl-substituted derivatives of the pyrimidine series (III) (Z = CH) and *s*-triazine series (III) (Z = N) also become effective light stabilizers when one or more *o*-hydroxyphenyl groups are introduced at the vicinal positions to the N atoms of the heterocycle. The absorption of high UV energy by the molecules of the light stabilizer results from their transition to an unstable tautomeric form with a quinonoid structure, which is easily transformed into the initial aromatic form with loss of energy in the form of radiation not giving rise to degradation of the polymeric molecule [23]. The most effective light stabilizers among the above-mentioned arylazines are the 4-alkyl derivatives (III) [24].

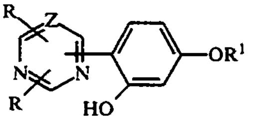


III

R = H, Alk, OAlk, $NAlk_2$, Ph
Z = CH or N

In addition to the fact that alkyl groups increase the compatibility of the photostabilizing additive and the polymeric substrate, thereby reducing the sweating effect, their presence in the benzene ring increases the absorption of UV radiation over the whole critical range of wave lengths for the polymer (290-400 nm) [25].

Such substituted pyrimidines (IV) (Z = CH) are used as protective agents against UV radiation in natural and synthetic polymeric products (fabrics, paper, resins, plastics, films, etc.) and in cosmetic and perfume compositions [24, 26].



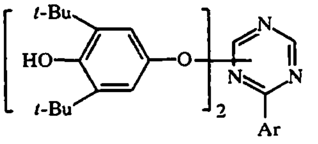
IV

R = H, CH_3, C_6H_5, $C_6H_3(OH)_2$-2,4, $C_6H_3(OH)$-2-(OR^1)-4
R^1 = H, CH_3...$C_{18}H_{37}$; Z = CH or N

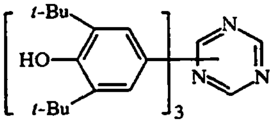
Similar protection against radiation is provided by the hydroxyphenyl derivatives of 3,3'-bipyridine, 5,5'-bipyrimidine [27, 28], and *s*-triazine (IV) (Z = N) [29]. Thus, elastic cine and photographic film containing 2% of *o*-hydroxyphenyl-*s*-triazine as light stabilizer remained unchanged after exposure for 1000 h, whereas film without such an additive was covered with cracks and became brittle [29]. A similar effect was achieved by the addition of the dihydroxyphenyl derivative of triazine

(IV) [Z = N, R = $C_6H_3(OH)_2$-2,4, R^1 = $CH_2COOC_2H_5$] to polyacrylate [30]. It was also shown that the photodegradation of low-density polyethylene was inhibited in the presence of small amounts of 2,4-dialkyl- or 2,4-diaryl-6-(*o*-hydroxyphenyl)-*s*-triazine [31]. 3,3'-Dihydroxy-2,2'-bipyridines also exhibit the characteristics of light stabilizers, and their phototautomerization involving two chelate hydrogen bonds takes place with a high quantum yield of fluorescence [32].

Polymers are also destroyed as a result of thermal degradation under the influence of heat and atmospheric oxygen with the formation of active radicals, the action of which leads finally to cleavage of the polymer chains. This process can be retarded by the addition of thermal stabilizers (antioxidants, acting as traps for the radicals that form) to the polymer. Derivatives of sterically hindered phenols are used as effective free-radical traps. They include aryl-substituted *s*-triazines (V) [33]. The triaryltriazine (VI), together with other phenolic compounds, has been recommended for the stabilization of the polyethylene coatings of copper wires and printed circuits [34].



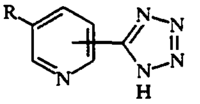
V



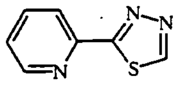
VI

The amino and aminophenyl derivatives of *s*-triazine may find use as stabilizers for oils [35] and polymeric materials [36, 37], as inhibitors of the corrosion of metals [36, 38], and as enhancers for the adhesion of polymeric coatings [39, 40].

Stabilizing characteristics are also exhibited by certain heteroarylpyridines, which are used in silver-halide black and white and color photography in developers and in photoemulsions together with other heterocyclic compounds, such as derivatives of imidazole, benzimidazole, benzothiazole, triazole, etc. Used as ingredients in multicomponent compositions, α- or γ-pyridyltetrazoles (VII), pyridylthiadiazoles (VIII), and α-pyridyltriazines (IX, X) stabilize photographic materials during development and processing at high temperature, inhibit fogging, improve the long-term storage of photographic materials, and increase the stability of the obtained images to the action of light [41-45].

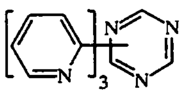


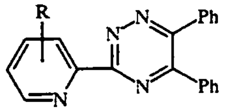
VII



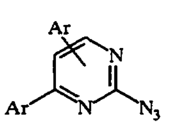
VIII

R = H, CH_3



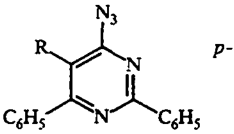


The introduction of the energy-rich azido group into the arylazine molecule makes it possible to use the instability of such compounds toward the action of light for the creation of photosensitive materials. It was suggested that aryl-substituted 2- and 4-azidopyrimidines (XI, XII) could be used as silver-free photorecording materials with physical development [46, 47].



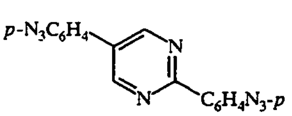
XI

Ar = C_6H_4Cl-*p*, $C_6H_4OCH_3$-*p*



XII

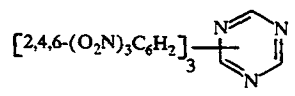
R = H, CH_3



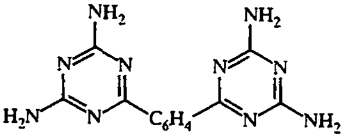
XIII

The same azidopyrimidines have found use in a new method for the formation of positive color images on porous substrates [48]. 2,5-Bis(*p*-azidophenyl)pyrimidine (XIII) was used as light-sensitive component in a process for the development of a latent image on a photoimmobilized support [49].

The accumulation of several nitro groups in the arylazine molecule leads to an increase in the energy content of the compound with retention of sufficient thermal stability. Thus, 2,4,6-tripicryl-*s*-triazine (XIV), which exhibits high stability toward heat without decomposition, was used as a model during determination of the characteristics of explosives and as an energy-containing component in the composition of rocket fuels [50, 51].

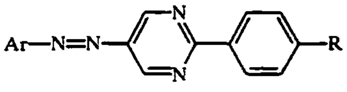


XIV



XV

Arylazines with an amine function in the heterocycle are interesting primarily as biologically active substances — their use in other respects is limited to isolated examples. Thus, 1,2-bis(2,4-diamino-*s*-triazinyl)benzene (XV) proved useful for the preparation of a charge-controlling composition, used in a high-grade electrostatic toner [52]. 2-Hydrazino-6-arylpyrimidine-4-carboxylic acids form the basis for the preparation of highly selective and sensitive indicator papers for the determination of Fe(II) and Fe(III) [53], while *o*-hydroxyphenyl-substituted 2- and 4-hydrazinopyrimidines were used for the preparation of reagent papers for the rapid semiquantitative determination of microquantities of metals (Cu, Co, Hg, Ni, Pd) [54, 55].

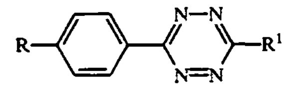


XVI

R = Br, CN, OCH_3, OC_4H_9, OC_6H_{13}, *p*-$C_5H_{11}C_6H_4$

Ar = *p*-AlkOC_6H_4, *p*-$(CH_3)_2NC_6H_4$, C_5H_{11}–N N–C_6H_4-*p*

Various dichroic dyes are used as liquid-crystalline materials in modern displays operating on the "guest—host" principle, and this makes it possible to achieve not only high clarity in the image but also to present data in color. Such dichroic materials include, for example, 5-arylazo-2-arylpyrimidines (XVI) with positive dichroism [56] and 6-substituted 3-aryl-*s*-tetrazines (XVII) with negative dichroism [57, 58], some of which may find practical application.



XVII

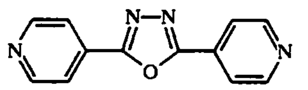
R = Alk, OAlk, C_6H_4Alk, C_6H_4OAlk, OC(O)Alk, OC(O)C_6H_4Alk, OC(O)C_6H_4OAlk

R^1 = Alk, NHAlk, N(Alk)$_2$

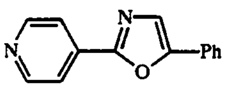
Some liquid-crystalline compounds of the azine series have found use as specific stationary phases in gas chromatography, making it possible to separate successfully, for example, difficultly separated isomers of hydrocarbons. Thus, 5-R-2-(*p*-R′-phenyl)pyrimidines (where R and R′ are C_nH_{2n+1}, $C_nH_{2n+1}O$, $C_nH_{2n+1}CO$, or $C_nH_{2n+1}COO$ with n = 1-12) can be used as stationary phases in gas-chromatographic columns [59, 60]. An example of the use of 2-(*p*-nonyloxyphenyl)-5-heptylpyrimidine in capillary gas chromatography for the separation of isomeric alkylbenzenes and alkenes is known [61]. Amphiphilic carboxy derivatives of phenylazines (pyridine, pyrazine, pyrimidine) with a $C_{12}H_{25}O$ group give well-packed Langmuir—Blodgett films with higher compression collapse values than a film from dodecyloxybiphenylcarboxylic acid [62].

No less important is the use of certain aryl- and heteroaryl-substituted pyridines as materials for nonlinear optics.

Compounds (XVIII-XX) find use in photoelectric instruments, photoconducting circuits, piezoelectric devices, light sources for laser printers, etc. [63-66]. Their quaternary salts, called laser dyes, are used in the form of solutions for the creation of the active medium [66]. A characteristic feature of the compounds is the presence of electron-donating groups,

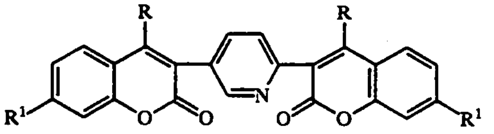


XVIII



(or p-C_6H_4-C_6H_5)

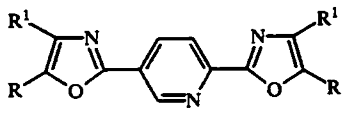
XIX



XX

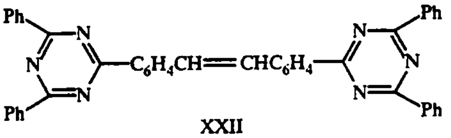
R, R^1 = Alk, $-NAlk_2$

conjugated with the heteroatom of the pyridine ring, in their structure, which makes it possible to accept energy conducted from outside and to convert it into laser radiation with possibly smaller losses. On account of the broad emission spectra of these dyes, smooth rearrangement of the laser emission wavelength is possible. The dyes have strong fluorescence. This property is also characteristic of the structurally similar 2,5-bis(2′-oxazolyl)pyridines (XXI) used as fluorescent whiteners for polymers [67], the derivatives of 3-cyano-4,6-diarylpyridines used as fluorescent dyes [68], and 4,4′-bis(*s*-triazinyl)stilbene (XXII) and 1-(2,4-dimethoxy-*s*-triazinyl)pyrene, which are fluorescent whiteners for polyester fibers [69, 70]. 2,4-Bis(1-anthraquinonyl)-6-phenyl-*s*-triazine belongs to a group of important paint pigments [70].



XXI

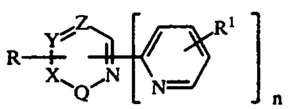
R, R^1 = H, CH_3, C_2H_5, C_6H_5, Ar



XXII

2. COMPLEXING PROPERTIES OF ARYLAZINES

An important characteristic of arylazines is their ability to form complexes which find practical use. Thus, 2-(4-methylphenyl)pyridine is used in the form of complexes with cobalt, copper, and nickel as coloring for polymers and for polystyrene in particular [71]. Among the ligands, the most important from the standpoint of their practical application are the azine systems (XXIII) containing α-pyridyl groups as substituents at the C atoms adjacent to the N-heteroatoms.



XXIII

X, Y, Z, Q = N or CH; n = 1, 2, 3

R = H, CH_3, C_6H_5, CN; R^1 = H, CH_3, $C_6H_4SO_3H$-p

Such α-pyridyl-substituted azines, and primarily 2,2′-bipyridines, have the ability to form stable and intensely colored chelate complexes with the ions of transition metals (Fe, Cu, Ni, Co, Mn, etc.). They are used in analytical chemistry for the separation and purification of various samples, materials, and media [72-76]. α-Pyridylazines exhibit high selectivity in complexation, and this is attributed to the rigidity of the aromatic system and the enhanced role of steric factors. Toward the metal ion, the α-pyridylazines act as ligands that supply the free electron pairs of the nitrogen atoms to the unoccupied orbitals of the metal cation; here the number of coordination bonds with the metal is determined by the number of electron-donating centers in the ligand. Their complexing abilities therefore show up considerably more strongly than in such substituted azines as, for example, 2-furylazines [77]. In this quality, some derivatives of α-pyridylazines have been proposed as agrochemical fungicides; it is suggested that their fungicidal activity is due to the formation of copper chelate complexes and to change in the bioavailability of the copper [78].

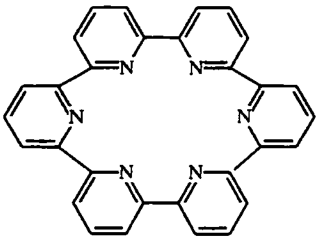
Although there is little information on the use and properties of α-pyridylazines as complexing agents, most of the information, its practical significance, and the extent of its application mostly concern 2,4,6-tris(α-pyridyl)-*s*-triazine (IX). This is probably due both to its synthetic availability and to the stability of the color of the complexes [79]. It is necessary to mention the use of this reagent in the determination of sulfur dioxide in the outgoing gases of various processes, based on the reduction of Fe(III) to Fe(II) and the formation of a violet chelate complex by the latter [80]. The same principle of complexation and subsequent spectrometry is used in analyses for iron, chlorine, and ascorbic and uric acids in such biological substrates as blood serum and plasma, urine, and protein-containing fluids and also in the determination of cholesterol in blood, adrenaline, and noradrenaline and similar compounds in medicinal preparations [81-86].

The determination of iron by means of the reagent (IX) is also used in the analysis of various inorganic subjects, e.g., aluminum, steels, metal specimens, ore "tailings," and sand [87-90]. The reagent is also used in the determination of copper, cobalt, cadmium, and nickel in alloys and in water and also for the separation of metals by selective extraction or adsorption. The extraction method was used for the separation of elements of the actinium and lanthanum group, and trace quantities of radioactive impurities were removed from effluents [91-94]. Active carbon impregnated with a mixture of compound (IX) and potassium iodide was used as adsorbent in adsorption separation. For example, trace quantities of copper and cadmium in samples with large iron and aluminum contents are separated on such a sorbent [95]. A sorbent based on tri(α-pyridyl)-*s*-triazine (IX) and sodium tetraphenylborate is used for the removal of small iron impurities from food products, wines, water, beer, nonalcoholic drinks, etc. [96]. The structurally similar 2,4,6-tris{2-[4-(*p*-sulfophenyl)]pyridyl}-*s*-triazine also makes it possible to determine trace quantities of iron in food products and microbiological preparations [97]. The quaternized form of tripyridyltriazine (IX) is proposed as an electrochromic material for displays [98]. The analog of (IX) 2,4,6-tris(γ-pyridyl)-*s*-triazine is of definite practical interest. However, to judge from published data, the scale of its use is not as large as that of its α analog. There are data on its possible use as an extractant for the removal of phenol from effluents [99], in epoxide resin compositions used for sealing vessels, for the manufacture of seals in electric and radio components [100], and in protective layers for electrophotographic materials [101].

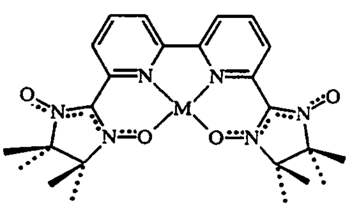
3-(α-Pyridyl)-*as*-triazines (X) are specific analytical reagents for Cu(I) [102-104], Co(II) [105,106], Ni(II) [107], Fe(II) [108-112], Pd(II) [113], and Ru(II) [114]. The best reagents for Fe(II) are considered to be disulfonic acids based on the 5,6-diphenyl derivative (X) (Ferrozine) [115] and its 5,6-difuryl analog (Ferene S) [116]. The triaryl derivative (X) (R = C_6H_5) is recommended for use in electrodeless coating with copper during the production of printing plates [117]. The β-pyridyl analog of compound (X) also proved suitable for the spectrophotometric determination of Fe(II) in aluminum alloys and powders [118].

Other practical uses are known for pyridylazines. The complexes of 2,3-bis- and 2,5-bis(α-pyridyl)pyrazines with Ru(II) are proposed for use as luminescent samples, many-electron catalysts, and components for photosensitive processes on account of the presence of broad and strong absorption bands in the visible region for these complexes, the relatively long luminescence, and the high reduction potential [119]. A special position is given to the complexes of 2,2′-bipyridine with Ru and Rh, which are effective homogeneous catalysts of the photodecomposition of water under the influence of sunlight for the production of hydrogen [120] and oxygen [120, 121] and the photoreduction of CO_2 to CO, methane, ethane, ethylene, and more complex organic compounds, depending on the nature of the complex and the presence of colloidal particles of Pt, Rh, Ru, and Os and other components [122].

It is possible to mention the use of 2,3-bis(α-pyridyl)pyrazine and 2,4,6-tris(α-pyridyl)-*s*-triazine as promoters in the catalysts during the production of alcohols from synthesis gas [123]. This process gives a mixture of C_1-C_4 alcohols with a relatively high content of ethanol. The complexes of 2,2′-bipyridine with iron catalyze the cyclodimerization of butadiene with the formation of cycloocta-1,5-diene and 4-vinylcyclohexene [124].



XXIV

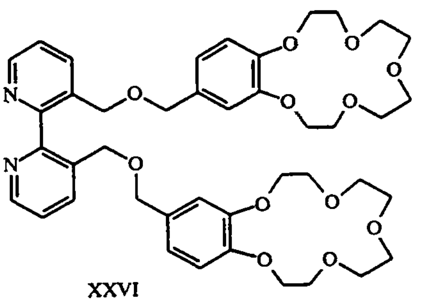


XXV

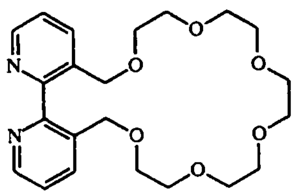
M = Cu(II), Ni(II)

Recently the attention of researchers has been attracted to the structure (XXIV), which is formed by six pyridine rings and has strong complexing characteristics [125].

The biradical di-N-oxyl derivative of 2,2'-bipyridine forms mononuclear chelate complexes (XXV) with Cu(II) and Ni(II), which are antiferromagnetic at ultralow temperatures [126]. The introduction of two benzo[15]crown-5 ether fragments at positions 3 and 3' of the 2,2'-bipyridine molecule makes it possible to construct the complexone (XXVI), in which the doubly charged diquat cation is easily inserted as "guest" between the two conformationally mobile polyether macrocycles [127].



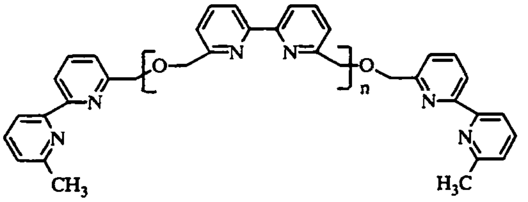
XXVI



XXVII

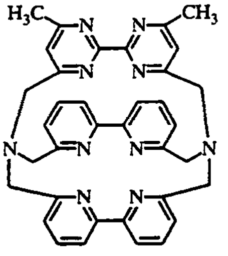
With the more sterically hindered conformation, which is found in the chelate complex of Ru(II) at the bipyridine nitrogen atoms of compound (XXVI), the insertion of the diquat molecule is no longer observed (the allosteric effect) [128]. A similar effect can be observed in the case of the polyether (XXVII), the size and flexibility of which change during the formation of complexes at the bipyridine nitrogen atoms with $PdCl_2$ and $W(CO)_6$ [125]. Conversely, during the formation of the complex of (XXVII) with $Hg(CF_3)_2$ the dissociation constant of the palladium complex with respect to the macrocycle is reduced by a factor of seven.

The presence of several azine fragments in the ligand makes it possible to construct supramolecular structures [129]. It was found that the reaction of the open bipyridine polyethers (XXVIII) with Ag(I) and Cu(I) gave helicates, consisting of two molecules twisted into a spiral and held together by several metal-chelate bonds [130, 131].



XXVIII

n = 1, 2, 3



XXIX

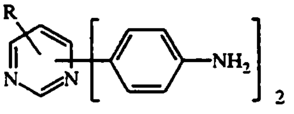
In the series of macrocyclic cryptands constructed from biheteryls the 2,2'-bipyrimidine analog (XXIX) may be of specific interest for molecular electronics. With Eu(III) it gives a cryptate, which exhibits luminescence with good absorption and emission characteristics [132].

3. ARYLAZINES AS MONOMERS AND THE POLYMERS OBTAINED FROM THEM

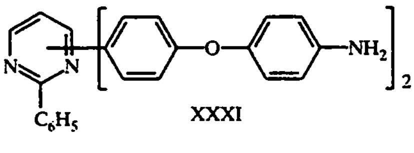
Of practical interest among arylazines are the diamino and triamino derivatives, capable in reaction with the dianhydrides of aromatic tetracarboxylic acids of forming the polymeric molecules of polyamidic acids. After chemical or thermal imidization, the products are transformed into high-molecular polyimides. Such aromatic polyimides (or polyarimides) number among the most promising types of organic polymers for modern technology, since they possess the highest thermal stability among all currently available organic materials and a range of other valuable technical qualities [133-136]. The demand for such materials is constantly increasing.

The high thermal stability, the good deformation—strength characteristics, the chemical inertness, the radiation stability, and the optimum dielectric properties characteristic of polyarimides of the benzene series are due to features of their chemical structure, i.e., the presence of alternating aromatic and imide rings in the main chain, the comparatively high degree of symmetry, and the strong intermolecular interaction of the polymeric chains [137]. One way of increasing the thermal stability is to introduce heterocyclic fragments, including representatives of the azine series (pyridine, pyrazine, pyrimidine, quinoxaline, triazine), into the main chain of the polyimides.

In contrast to the purely aromatic compounds, the polyarimides containing heterocyclic fragments withstand higher temperatures [135]. The 2,4-, 2,5-, and 4,6-bis(*p*-aminophenyl)pyrimidines (XXX) and also those with phenyl groups in the pyrimidine ring gave polymeric materials (films and fibers) with thermal stability appreciably exceeding the thermal stability of the polyimide materials based on aromatic diamines and widely used in industry [133, 138, 139]. Polyimides (XXXI) based on 2-phenyl-4,6-bis(*p*-aminophenoxyphenyl)pyrimidine were also synthesized [140].

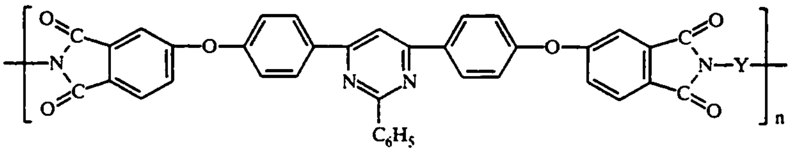

XXX

R = H, C_6H_5

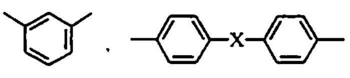

XXXI

The polyimides based on 2,4- and 4,6-bis(*p*-aminophenyl)pyrimidines have fairly close deformation—strength characteristics. At the same time, the polyimides from 2,5-bis(*p*-aminophenyl)pyrimidine have higher strength characteristics than the other pyrimidine-containing polyimides, due to the linear structure of the 2,5 isomer. It is also significant that these polyimides also have the highest thermal stability [138]. Thus, the tensile strength (σ) of polyimide films obtained from these diamines and pyromellitic dianhydride (polypyromellitimides, PPI) amounts to 151, 226, and 243 MPa respectively for the 2,4, 4,6, and 2,5 isomers. The same films from PPI have an elasticity modulus (*E*) of 3.10 GPa for the first two isomers and 8.44 GPa for the last [138, 140]. From comparison of published data [138-140], it follows that the strength characteristics of the polyimides are reduced if there is a phenyl substituent in the heterocycle compared with the unsubstituted analogs.

The inclusion of the pyrimidine fragment in the dianhydride component leads to the polyimides (XXXII), which are inferior in strength but superior in thermal stability to the polyimides in which the same fragment is in the diamine component [140, 141].

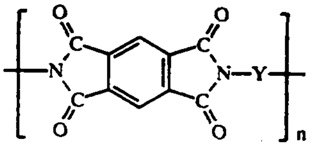

XXXII

Y =

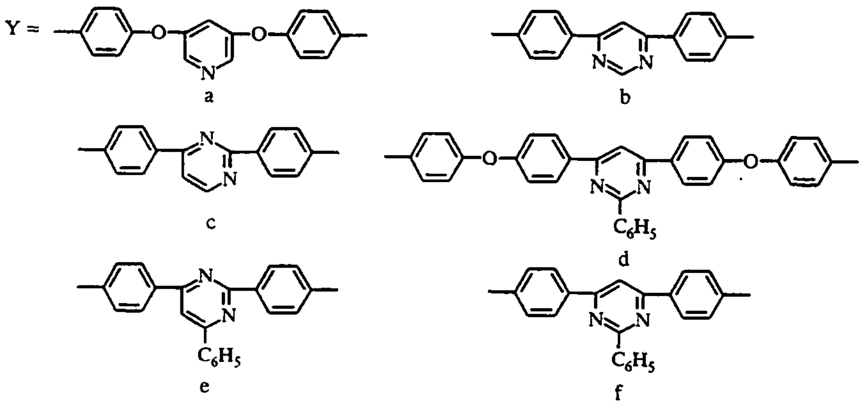


X = O, OC_6H_4O, CH_2, S, SO_2 etc.

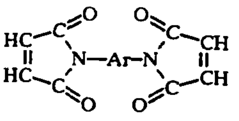
A comparative study of the thermooxidative stability of the heterocyclic polypyromellitimides (XXXIII) showed that the thermal stability of the polyimide chains is increased with "saturation" of their aromatic and heteroaromatic rings [141]. Thus, the temperature at which the PPI loses 5% of its mass is 340°C [in the case of (XXXIIIa)], 450°C [(XXXIIIb)], and 460°C [(XXXIIIc)] and increases to 490°C [for (XXXIIId)] and 540°C [(XXXIIIe, f)]; for the pyrimidine polypyromellitimides (XXXIIId-f) loss of 50-70% of the mass is observed at temperatures above 600°C, whereas for the others this usually occurs at 500-600°C [141]. In (XXXIIId-f) the pyrimidine rings are "concealed" within the macromolecule by the bulky phenyl substituents, and this inhibits the oxidation processes. The absence of phenyl substituents in the polymeric chains of (XXXIIIb) and (XXXIIIc) appreciably reduces their thermal stability. A similar result was obtained for polyimides based on the same diamines and oxydibenzenetetracarboxylic dianhydride [141].



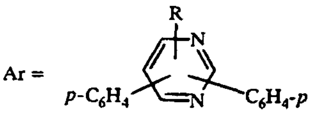
XXXIII



The most complete information on the application of heterocyclic diamines as monomers for the production of polymers has been given for 2,5-bis(aminophenyl)pyrimidine. Polyimide films and fibers with high strength and high thermal stability were obtained from it [142-144]. The outstanding strength characteristics of the polyimides are explained by a feature of their supramolecular structure, i.e., the high packing density of the polymer chains due to specific intermolecular contacts with displacement stacking of the polyimide chains and the pyrimidine rings [145, 146].

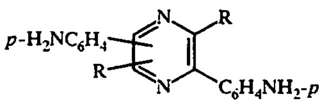


XXXIV



R = H, C_6H_5

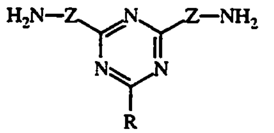
Bis(aminophenyl)pyrimidines are also used in the synthesis of unsaturated derivatives of aromatic diamines — N,N′-bismaleimides (XXXIV). They form the basis of a different approach to the creation of heat-resistant polymers, involving the addition of the diamines at the double bonds of bismaleimide and subsequent polymerization with the formation of cross-linked three-dimensional structures without the release of volatile products. This makes it possible to produce nonporous bulky components [147]. The inclusion of heteroaromatic fragments in the main polymer chain secures the optimum thermal stability and mechanical strength for the polymer.



XXXV

R = H, CH_3

Like the pyrimidine analogs (XXX), aryl-substituted pyrazines with aminophenyl groups at positions 2,5 or 2,6 of the pyrazine ring (XXXV) are suitable for the production of heat-resistant polyimides [148] and as hardeners for epoxy resins [149]. Bis(aminophenyl)-*s*-triazines (XXXVI) are widely used for the production of molding powders, films, and laminar plastics having high heat resistance and strength [150, 151]. A polyimide film based on 2-phenyl-4,6-bis(*p*-aminophenyl)-*s*-triazine retains its mass when heated to 530°C, remains flexible, and does not break after 1560 h trials at 300°C [150]. There are also data on the production and properties of polyimides containing a triazine ring in the dianhydride fragment [151-153].


XXXVI

$Z = m\text{-}, p\text{-}C_6H_4$, cyclo-Alk, $p\text{-}C_6H_4\text{-}X\text{-}C_6H_4\text{-}p$

$X = O, S, SO_2, CH_2, CO, CHAlk, CHAr$

$R = C_6H_5, NHC_6H_5, N(Alk)C_6H_5, N(Ar)C_6H_5$

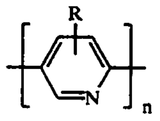
The thermal characteristics of the polyether and polyamides obtained by the polycondensation of 2-phenoxy-4,6-bis(*p*-chlorocarbonylphenyl)-*s*-triazine with ethylene glycol, *p*-phenylenediamine, and hexamethyldiamine were studied. It was noticed that the presence of the oxygen bridge between the triazine ring and the carboxyphenyl group leads to a decrease in the heat resistance and thermal stability of the polymers [153], as was observed for the polyimides from 2,5-bis(*p*-aminophenoxy)-4,6-diphenylpyrimidine [154] and 2,5-bis(*p*-aminophenyl)diphenylpyrimidine [138]. The aromatic polyethers obtained by the copolymerization of bis(hydroxyphenyl)pyrimidines with hydroxyphenyl sulfones have reduced viscosity, good solubility in organic solvents, high softening temperatures, and sufficient thermal stability [155].

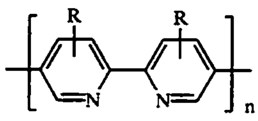
In the pyridine series, bis(aminophenyl)pyridines are known [156], but there are no data on their use for the production of polymers. Only the structurally similar monomers 2,6- and 3,5-bis(aminophenoxy)pyridines [141, 157], 4,4'-diamino-2,2'-bipyridine [158], phenylenebis(hydroxypyridylamines) [159], and also 2,3,5,6-pyridinetetracarboxylic and 3,5-bis(3',4'-dicarboxyphenoxy)pyridinecarboxylic dianhydrides [160] have been used in the synthesis of polyimides.

Comparison of the thermal characteristics of the polyimides obtained from aromatic diamines and bis(aminophenyl)azines demonstrates the advantages of the latter. This superiority in thermal stability over the purely aromatic polyimides makes it possible to use such polymers for the production of fibers, films, adhesives, and compositions with construction materials capable of operating at elevated temperatures [161].

From 3,6-bis(*p*-fluorophenyl)pyridazine and bisphenol A, a different type of polymer was obtained with a heteroaromatic fragment in the main chain — polyaryl ethers of the pyridazine series [162]. The possibility of using 4-(2,4-dichloro-*s*-triazinyl)styrene and bringing it into copolymerization with styrene, leading to the production of a polymer with active chlorine atoms, was also demonstrated [163]. Diaminotriazines with phenyl [164] or imidazolyl [165] groups in the triazine ring can be brought into polymerization with formaldehyde and phenol for the preparation of polymeric coatings [164] and into reaction with epoxy compounds for the hardening of resins [165].

π-Conjugated polymers consisting of 42-300 monomer units of pyridine (XXXVII) and bipyridine (XXXVIII) and having a strictly rod-like structure have unique properties [166].


XXXVII


XXXVIII

Thus, an extended film of polyvinyl alcohol coated with these polymers has the properties of an optical polarizer with a high dichroic ratio. Dilute solutions of poly(2,5-pyridinediyl) and poly(2,2'-bipyridine-5,5'-diyl) have fluorescence, and the color changes from yellow to blue during *p*-complexation. In addition, some of these complexes with Ru(II), Ni(II), Ni(0), and Fe(III) catalyze the photorelease of hydrogen from water and the reduction of CO_2 [166]. The production of polyheteroarylenes containing the *as*-triazine fragment in the main chain has been reported [135].

Bischloromethyl and bistrichloromethyl derivatives of aryl-*s*-triazines have found use in polymer chemistry as polymerization initiators [167-169]. They can be used as compositions for recording optical data during photolithography [170-174], for recording holograms [175], in electron-beam resistors during the production of semiconducting devices [176, 177], in photosensitive compositions for the production of visible [172, 178] or negative images [179], in the formation of microcapsules for liquid-crystal displays [180], and in light- and heat-sensitive recording materials [181].

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