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A General Method of the Synthesis of "Step-Ladder" Polymers*)

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SUMMARY:

A new general method for the synthesis of "step-ladder" polymers was developed. It involves the interaction of aromatic diamines, containing in *o*-positions aromatic heterocycles with reactive hydrogen atoms, with aromatic dicarboxylic acids or their derivatives. This general method was used for the preparation of new classes of thermally stable polymers of type **27, 28, 29** and **30,** containing 1,2,4-triazole-, 1,2,4-triazolo[4,3-*c*]-quinazoline-, benzimidazole- or benzimidazolo[1,2-*c*]quinazoline-rings. Physical properties of these polymers were determined together with those of corresponding model compounds.

ZUSAMMENFASSUNG:

Eine neue generelle Methode zur Synthese von „Step-ladder"-Polymeren wurde entwickelt. Dabei werden aromatische Diamine, die in *o*-Stellungen durch aromatische Heterocyclen mit reaktivem Wasserstoff substituiert sind, mit aromatischen Dicarbonsäuren oder deren Derivate umgesetzt. Diese generelle Methode wurde zur Darstellung neuer Klassen thermisch stabiler Polymerer des Typs **27, 28, 29** und **30** verwendet, die 1,2,4-Triazol-, 1,2,4-Triazolo[4,3-*c*]chinazolin, Benzimidazol- oder Benzimidazolo[1,2-*c*]chinazolin-Ringe enthalten. Die physikalischen Eigenschaften dieser Polymeren sowie entsprechender Modellverbindungen wurden bestimmt.

Synthesis of polymers having a "ladder" or "step-ladder" structure is one of the ways to increase the thermostability of heterocyclic polymers[1,2].

At the present time two general methods of synthesizing such polymeric systems find the most extensive applications. One of the methods combines homo-polycondensation ($XY = Z$) and hetero-polycondensation of tetrafunctional compounds and proceeds in two stages forming at the first stage linear repeating units and at the second stage heterocyclic repeating units according to the following general scheme:

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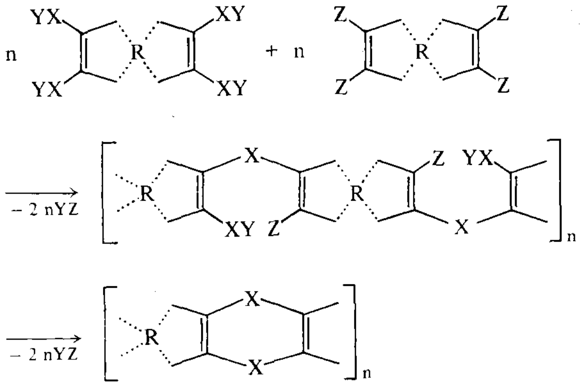
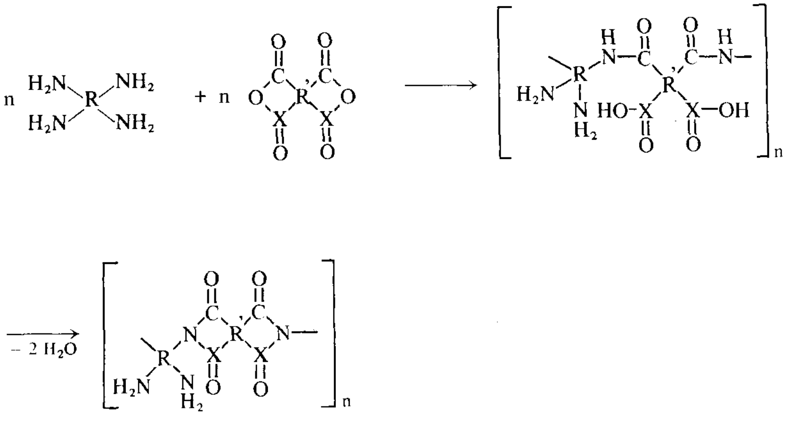
*) Presented at the XXIVth IUPAC Congress, Hamburg, 1973.

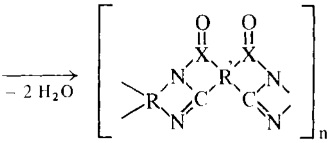


The synthesis of polydihydrophenazines by homocondensation of bis(*o*-phenylenediamines)[3, 4] or the synthesis of polyquinoxalines from bis(*o*-phenylenediamines) and tetraketones[5, 6] etc., are the most typical examples of such reactions.

The other method of synthesizing "step-ladder" and "ladder" polymers consists of a three-stage polycyclocondensation of aromatic tetraamines or their analogues with aromatic tetracarboxylic acids, or their derivatives and analogues.

At the first stage of the reaction *o*-substituted polyamides are formed. The second stage affords *o*-substituted polyimides or their analogues, and at the third stage heterocyclic polymers with a "ladder" structure are usually formed. The general scheme of polymer synthesis by this method using tetracarboxylic acid dianhydrides can be described as follows:

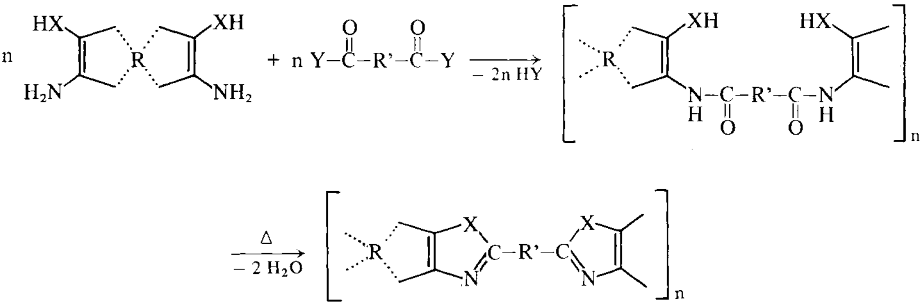




X = C, S, SO

This method is widely used to prepare polymers such as poly(aroylenebenzimidazoles)[7], poly(aroylene-*s*-triazoles)[8], poly(isoindoloquinazolinediones)[9] etc.

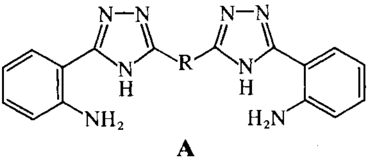
In 1968 we proposed a new general synthetic method for "step-ladder" polymers. The procedure is based on the two-stage polycyclocondensation of dicarboxylic acids or their derivatives with aromatic diamines containing aromatic heterocycles with reactive hydrogen atoms at the *o*-positions to the amino groups[10]. This method is a modification of the well-known general method for the synthesis of polybenzazoles[11] based on the two-stage interaction of dicarboxylic acids or their derivatives with aromatic diamines containing hydroxy, mercapto, amino and other groups with reactive hydrogen atoms at the *o*-position of amino groups. At the first stage polyamides are formed containing substituents with reactive hydrogen atoms at the *o*-positions of the amide units, preformed for a condensation with the elimination of water and the formation of the benzazole cycle at the second stage:



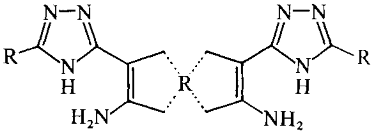
X = O, S, NC_6H_5 etc.

After the substitution of hydroxy, mercapto and amino groups by aromatic heterocycles with reactive hydrogen atoms in the starting nucleophiles the possibility of cyclization remains. In this case higher condensed heterocycles are formed, which accounts for a "step-ladder" structure of the final polymers.

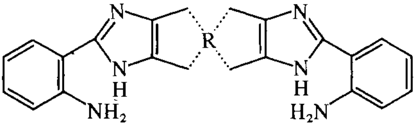
As such heterocycles 1,2,4-triazole or benzimidazole rings were incorporated in the starting diamines of the following general formulae:



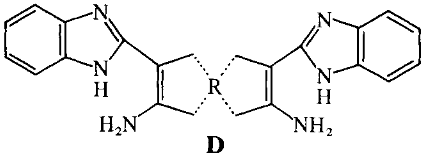
A



B



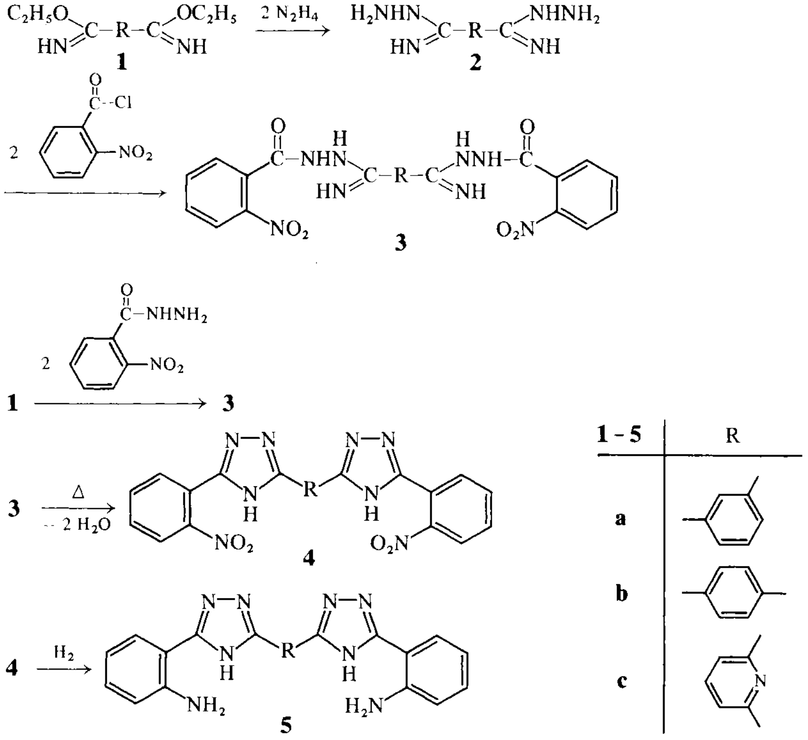
C



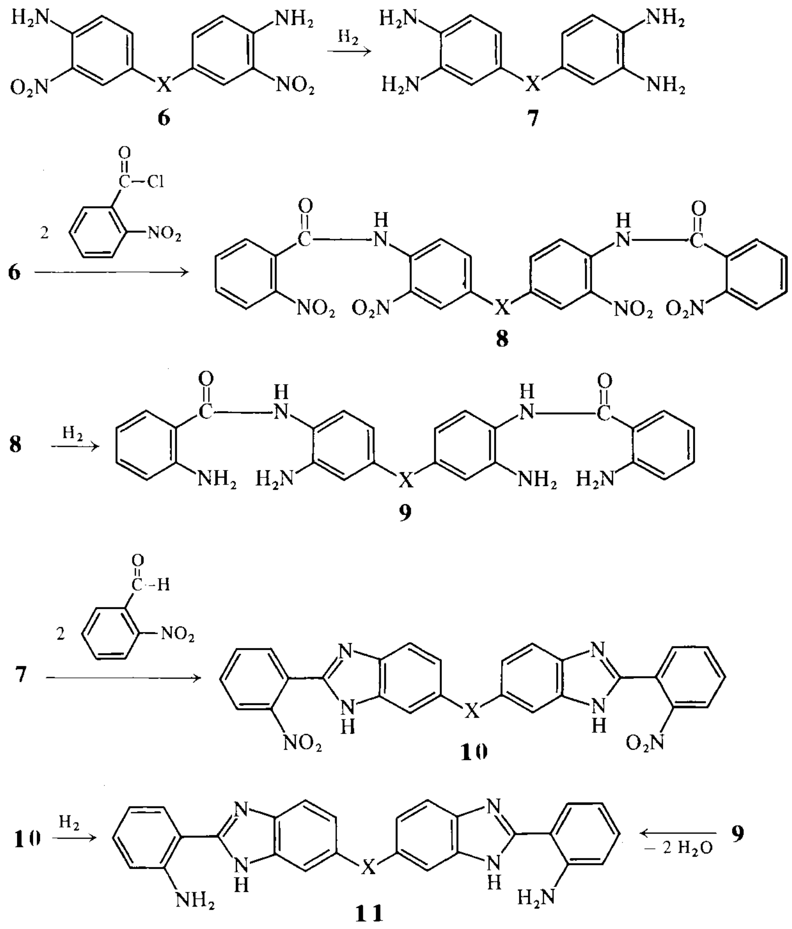
D

In the course of this investigation the synthesis of "step-ladder" polymers based on the diamines of type **A** and **C** has received primary emphasis.

The diamines of type **A** (bis[5-(*o*-aminophenyl)-1,2,4-triazole-3-yl] arylenes) were synthesized by two methods according to the following general scheme:



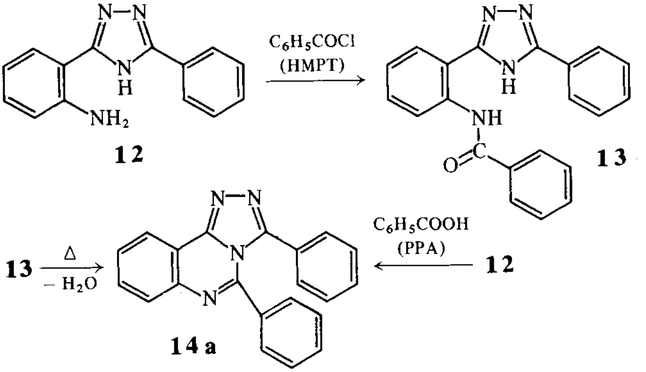
The diamines of type **C**, bis[2-(*o*-aminophenyl)benzimidazole-6-yl]derivatives were synthesized by two methods[15] according to the following general scheme:



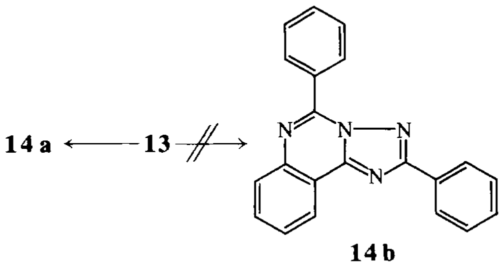
6-11	a	b
X	—	–O–

The general properties of the diamines and intermediates synthesized are represented in Tab. 1 (Exptl. Part).

The synthesis of polymers based on diamines of type **A** and type **B** was preceded by the investigation on several model reactions[13-15] to determine the optimum conditions of the synthesis of polymers and their structure. The simplest model compounds based on 1,2,4-triazolyl substituted amines, 3-phenyl-5-(*o*-benzoylaminophenyl)-1,2,4-triazole (**13**) and 3,5-diphenyl-1,2,4-triazolo[4,3-*c*]quinazoline (**14a**) were obtained by the reaction of 3-phenyl-5-(*o*-aminophenyl)-1,2,4-triazole (**12**) with benzoylchloride in hexamethyl phosphoric acid triamide (HMPT) followed by thermal cyclodehydration or by the reaction of **12** with benzoic acid in polyphosphoric acid (PPA)[12-14,18].

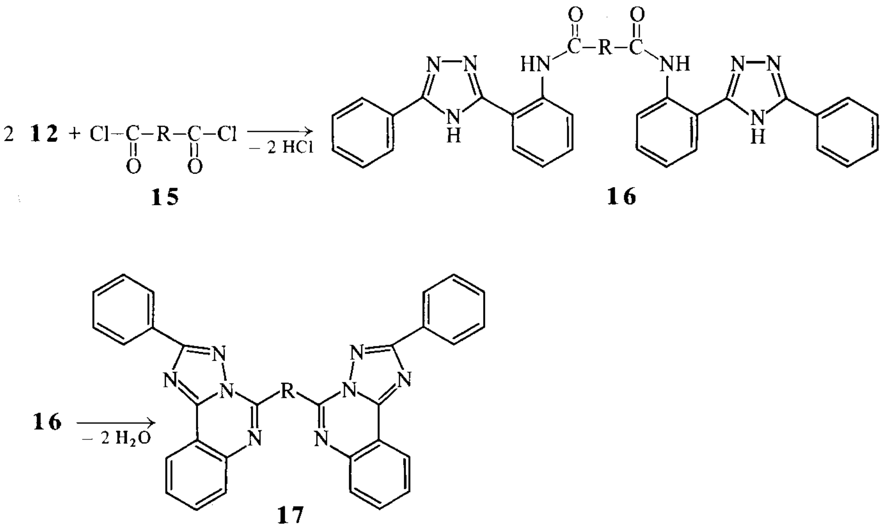


The cyclodehydration of **13** can lead to the two isomeric compounds **14a** and **14b**:



However, we succeeded in isolating but one cyclodehydration product which is supposed to have structure **14a**.

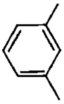
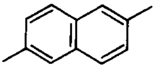
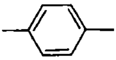
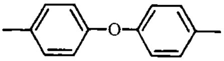
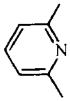
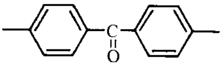
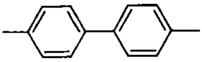
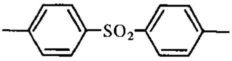
More complex model compounds were prepared by the reaction of **12** with aromatic dicarboxylic acid dichlorides **15a–h** in HMPT followed by thermal cyclodehydration of the reaction products:



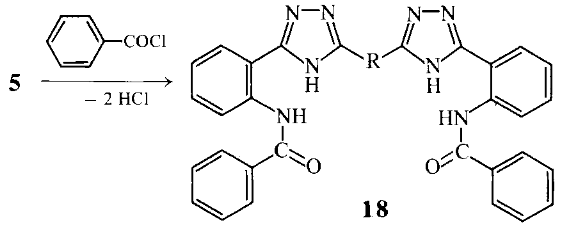
15

16

17

15–17	R	**15–17**	R
a		**e**	
b		**f**	
c		**g**	
d		**h**	

or by the reaction of compounds **5** with benzoyl chloride in HMPT followed by heating the reaction products:



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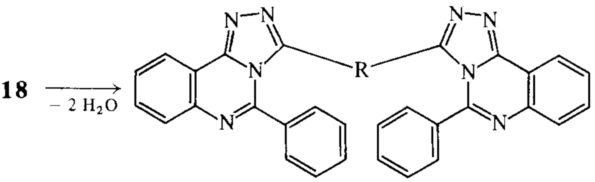
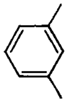
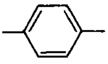
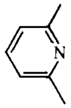


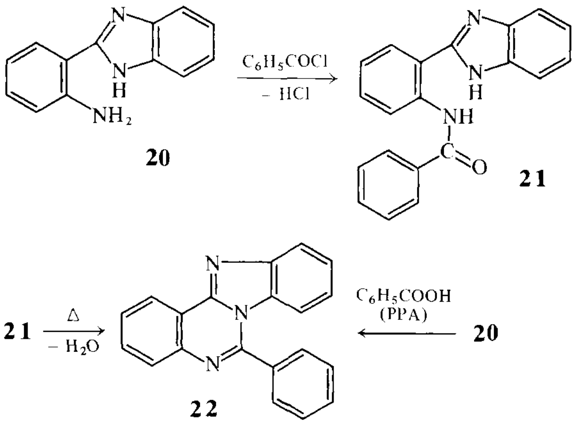
19

18, 19	R
a	
b	
c	

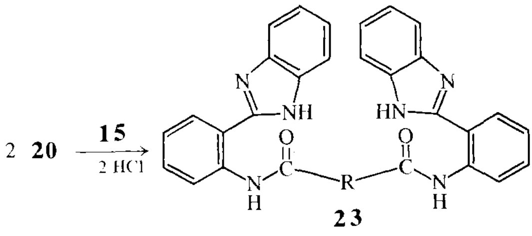
The structure of all model compounds was confirmed by elemental analysis, IR and UV spectra (Tab. 2a–d, Exptl. Part). The IR spectra of all *o*-acylaminophenyl-1,2,4-triazoles have absorption maxima characteristic for the amide carbonyl group (1640–1670 cm^{-1}), for the NH of the amide group, and of the triazole cycle (2800–3400 cm^{-1}). In the course of cyclodehydration these maxima disappeared, and maxima at 1380 cm^{-1} characteristic of the tertiary nitrogen atom of the triazoloquinazoline cycle appeared. As shown by UV spectroscopic analysis, the cyclization was accompanied by increasing absorption intensity indicating the formation of systems with a higher degree of conjugation.

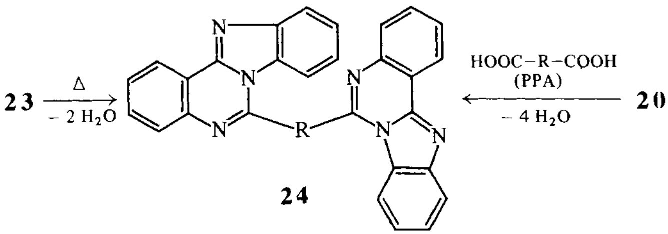
Some phys. properties of the model compounds are represented in Tab. 2a–c (Exptl. Part). It should be noted that the curves of differential thermal analysis of all bis(triazoloquinazoline)s show two exothermal processes, which is indicative of the degradation of the compounds in two stages.

The simplest model compound of the polymers based on 2-(*o*-aminophenyl)benzimidazole (**20**), 6-phenylbenzimidazo[1,2-*c*]quinazoline (**22**), was obtained by the reaction of **20** with benzoic acid in PPA or with benzoyl chloride in HMPT followed by thermal cyclization of the resulting 2-(2-benzoylaminophenyl)benzimidazole (**21**).

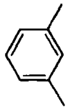
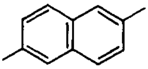
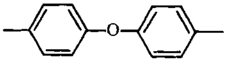
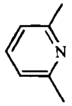
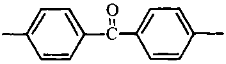
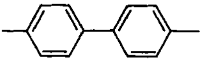
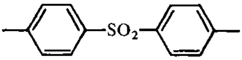


The more complex model compounds **24** were prepared by the reaction of **20** with dicarboxylic acid dichlorides in HMPT followed by thermal cyclodehydration of the resulting *N*,*N*′-bis[2-(benzimidazol-2-yl)phenyl]arylendicarboxamides (**23a–h**) or by the reaction of **20** with dicarboxylic acid or their derivatives in PPA.

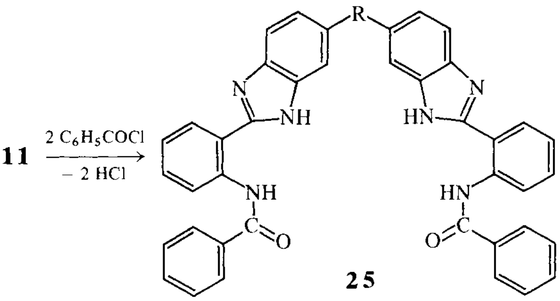




24

23, 24	R	**23, 24**	R
a		**e**	
b		**f**	
c		**g**	
d		**h**	

Other model compounds, 6,6′-diphenyl-3,3′-bi[benzimidazolo[1,2-*c*]quinazoline] (**26a**) or bis(6-phenylbenzimidazolo[1,2-*c*]quinazole-3-yl) ether (**26b**), were obtained from **11a** or **11b**, respectively, and benzoic acid under the conditions of the one stage cyclocondensation in PPA or in a two stage process condensation in HMPT followed by a solid phase cyclization of the resulting *N*-benzoyl derivatives **26a** or **b**, respectively:



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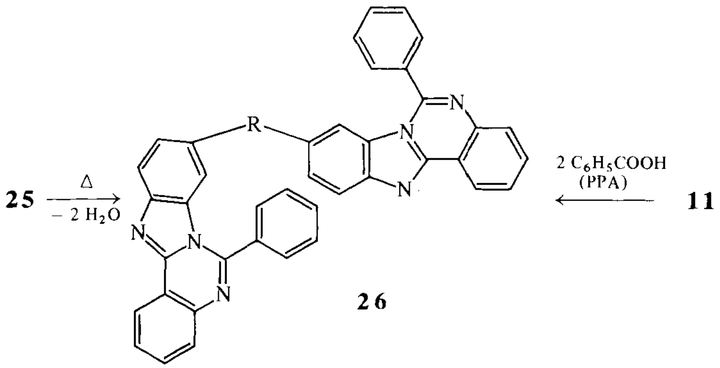
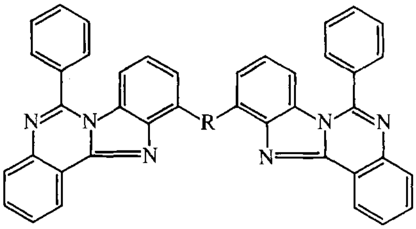


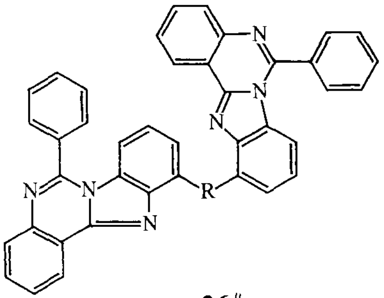
25, 26	a	b
R	—	–O–

The structure of the model compounds was confirmed by elemental analysis, UV (Tab. 3a, b, Exptl. Part) and IR spectra.

Some characteristics of these model compounds are given in Tab. 3a (Exptl. Part). It should be noted that compounds **24a–h** have sharp and high melting points, whereas compounds **26a, b** melt at lower temperatures with some interval. This is probably due to the fact that the latter are not pure compounds but are mixed with their isomers of the following structures **26′** and **26″**



26′



26″

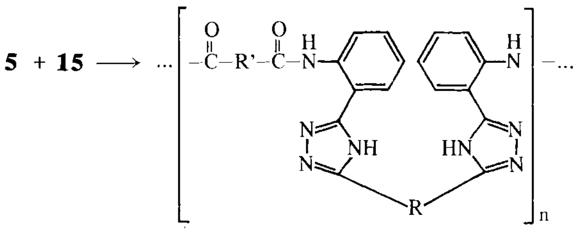
Investigations on the thermostability of the resulting model compounds by differential thermal and thermogravimetric analysis showed that these compounds begin to decompose vigorously at temperatures >400 °C. According to the differential thermal analysis data, the decomposition proceeds in two stages, the temperatures of maximum decomposition rates of these compounds being considerably higher than those of the above-mentioned bis(triazoloquinazoline)s.

Polymers based on diamines of type **A** and dicarboxylic acids, poly(triazoloquinazoline)s, were synthesized by a one-stage polycyclocondensation in PPA and a two-stage polycondensation according to the scheme below.

At the first stage of the two-stage process polymeric *N*-acylamino derivatives of **5**, polymers **27a–x**[*], were synthesized by low-temperature polycondensation of **5a–c** with **15a–h** in HMPT in the presence or absence of lithium chloride.

If the polycondensation was carried out in other polar aprotic solvents, dimethylacetamide, *N*-methyl-2-pyrrolidone etc., the polymers with more rigid chains separated from the reaction solutions, which prevented high conversion degrees in these processes.

The structure of the resulting polymers was confirmed by elemental analysis and by comparison of their IR and UV spectra with those of the corrresponding model compounds (Tabs. 2 and 4).



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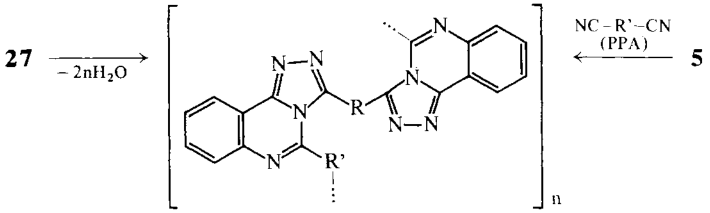

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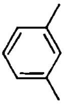
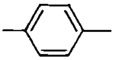
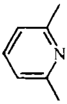
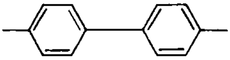
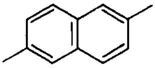
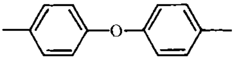
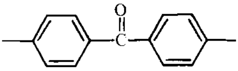
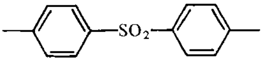
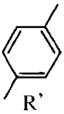
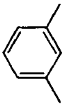
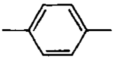
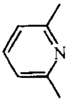
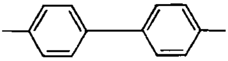
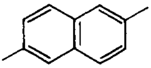
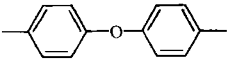
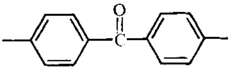
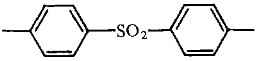
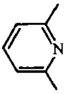
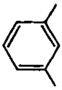
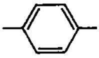
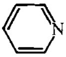
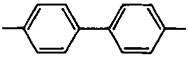
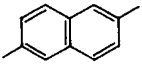
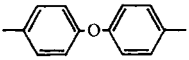
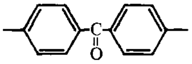
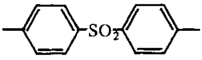
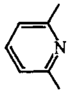
[*] According to "IUPAC", Information Bulletin No. 29, Nomenclature of Regular Single-Strand Organic Polymers, 1972: Poly(triazole-3,5-diylarylenetriazole-3,5-diyl-1,2-phenyleneiminocarbonylarylenecarbonylimino-1,2-phenylene)s.

27, 28	R =  R'
a	
b	
c	
d	
e	
f	
g	
h	

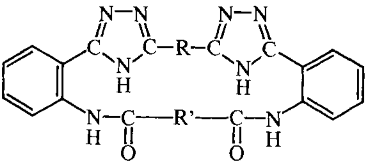
27, 28	R =  R'
i	
j	
k	
l	
m	
n	
o	
p	

27, 28	**q**	**r**	**s**	**t**	**u**
R' R = 					

27, 28	**v**	**w**	**x**
R'			
R = 			

The polymers **27a–x** are powdery white to light brown substances, soluble in HMPT, trifluoroacetic acid, formic acid and sulfuric acid depending on their structure.

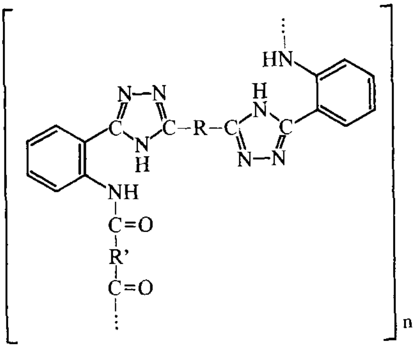
Rather lower viscosities of the resulting polymers ($\eta_{red.}^{25°C}$=0,28–0,72 dl/g), indicative for a relatively low degree of polymerization, may be attributed both to low nucleophilities of the diamines used and to the possibility of forming, along with linear macromolecules, various macrocycles, the simplest of which being represented as follows:



Brittle films were cast from the polymer solutions due to the low viscosities.

X-ray analysis of polymers **27** showed that they are partially crystalline, which points to some structural regularity of these systems irrespective of the asymmetry of their macromolecules.

This regularity can be explained by the predominant *transoidal* structure of the macromolecules of **27**:



Polymers **27** begin to soften in the range of 300–350 °C (from the thermomechanical analysis), differential and integral thermogravimetric analysis showed that these polymers reveal a weight loss in the temperature ranges of 60–150, of 300–350 and >475 °C. The weight loss at 60–150 °C is probably connected with the release of adsorbed moisture, that at 300–350 °C with the cyclization of the *o*-acylaminophenyl-1,2,4-triazole units to triazoloquinazoline units with the formation of poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diylarylene-1,2,4-triazolo[4,3-*c*]quinazoline-3,5-diylarylene)s (**28a–x**) and that at 470 °C with the decomposition of poly(triazoloquinazoline)s (**28**).

The general properties of polymers **27** are given in Tab. 4a–c (Exptl. Part). Cyclodehydration of **27** to **28** was carried out under vacuum ($\approx$0,5 mbar) at a maximum temperature of 350–375 °C for 12 h. Cyclization conditions are given in the Exptl. Part.

The structure of **28** was confirmed by elemental analysis as well as by comparison of the UV and IR spectra with those of the model compounds (Tab. 5a–c, Exptl. Part).

As in the case of the model compounds the cyclization of **27** to **28** is accompanied by the disappearance of an absorption maximum in the IR-spectra which is ascribed to the amide bonds and —NH-groups of amide and triazole cycle (1 640 – 1 670 and 2 800–3 400 cm^{-1}), as well as by the appearance of a maximum at 1 380 cm^{-1}, ascribed to the tertiary nitrogen atom. According to the data of the UV spectral analysis the cyclization is accompanied by an increasing absorption intensity which suggests the formation of polymers with a higher conjugation system.

According to the X-ray analysis data, the cyclization is accompanied by an increasing structural regularity.

The resulting poly(triazoloquinazoline)s **28** are brown powdery substances soluble in trifluoroacetic and sulfuric acids. $(\eta_{sp}/c)^{25\,°C}$ of 0,5% solutions in sulfuric acid are 0,20–1,02 dl/g (Tab. 5a–c).

Polymers with higher solution viscosities were obtained by a one-stage polycyclocondensation of **5** with aromatic dinitriles. $(\eta_{sp}/c)^{25\,°C}$ of 0,5% polymer solutions in H_2SO_4 were as high as 0,8–1,5 dl/g.

As shown by thermomechanical curves, these polymers soften in the range of 400–450 °C.

Some characteristics of **28** obtained by the two-stage method are given in Tab. 5.

Decomposition temperatures of **28** were determined by dynamic and isothermal thermogravimetry in air. According to the dynamic thermogravimetry

(ΔT=4,5 °C/min) the polymers begin to decompose in air (weight loss = 10%) at 460–550 °C. Some results of the dynamic thermogravimetry analysis are listed in Tab. 5.

According to the isothermal thermogravimetry (in air, 10 h), the polymer **28j** reveals a weight loss of only 8% at 425 °C, at higher temperatures strong pronounced decomposition takes place (Fig. 1a). A comparison of polymers **28b**, **28j**, and **28r** obtained from various diamines and terephthaloyl chloride (Fig. 1b), showed that the thermal stability of the polymers decreases depending on the diamine residue in the following order:

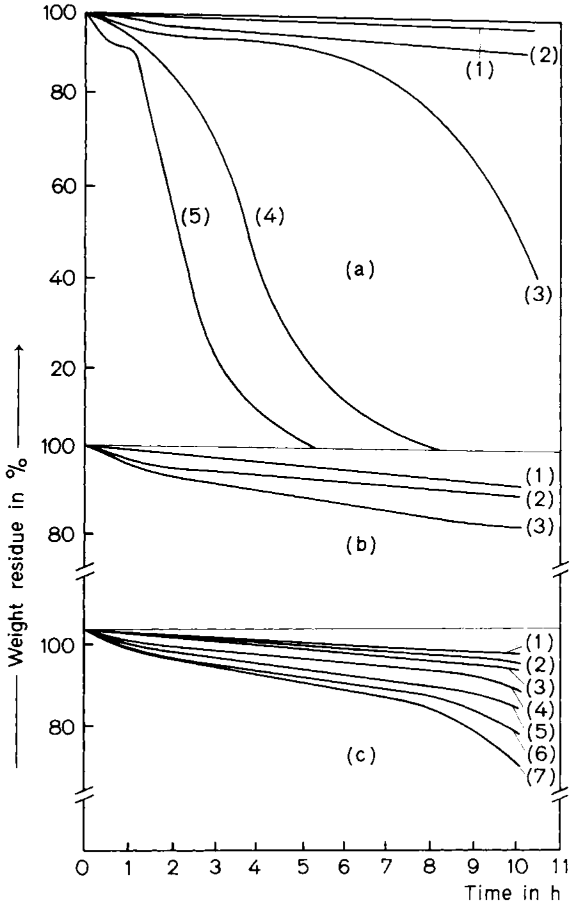
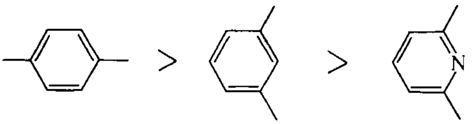


Fig. 1. Curves of isothermal thermogravimetry (in air, 10 h).

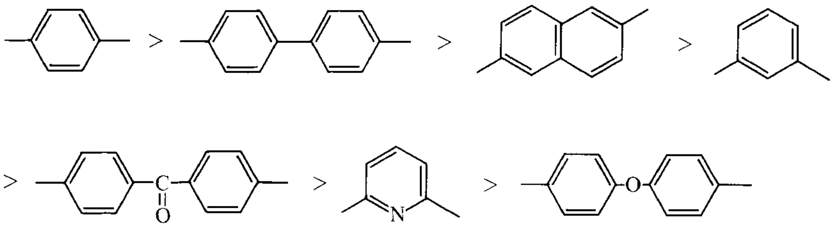
(a) Poly(triazoloquinazoline) **28j** at 400 °C (1), 425 °C (2), 450 °C (3), 475 °C (4), 500 °C (5)

(b) poly(triazoloquinazoline)s **28b** (1), **28j** (2), and **28r** (3) at 425 °C in air

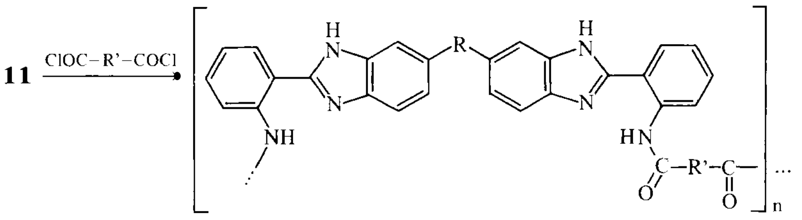
(c) poly(triazoloquinazoline)s: **28e** (1), **28i** (2), **28l** (3), **28m** (4), **28o** (5), **28f** (6), **28n** (7) at 425 °C in air



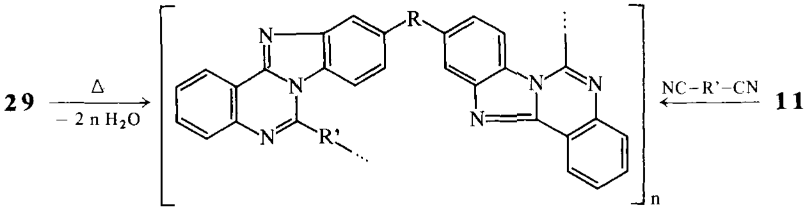
A comparison of the polymers obtained from 1,3-bis[5-(*o*-aminophenyl)-1,2,4-triazole-3-yl]benzene (**5a**) and various dicarboxylic acid dichlorides (Fig. 1c) showed that the introduction of flexibilizing groups in the macromolecules would lead to a considerable decrease of thermostability of the polymers, which agrees well with the results obtained previously[23]. The investigation of the influence of the acid residue on the stability of **28** showed that the thermostability of the polymers decreases in the following order:



Poly(benzimidazoloquinazoline)s, poly(benzimidazolo[1,2-*c*]quinazoline-2,6-diylarylenebenzimidazolo[1,2-*c*]quinazoline-6,2-diylarylene)s (**30**), have a thermostability still higher than poly(triazoloquinazoline)s **28**. They were obtained via **29** and the latter by the reaction of **11a, b** in HMPT with aromatic dicarboxylic acid chlorides. Similar to the synthesis of **28**, these polymers may also be prepared by a one-stage polycyclocondensation of **11** with dinitriles in PPA.



29



30

The structure of **30**, prepared by the two methods was confirmed by elemental analysis as well as by comparison of the UV and IR spectra with those of the corresponding model compounds.

The values of $\eta_{\text{red.}}^{30^\circ C}$ of the 0,5% H_2SO_4 solutions of **30** were found to be 0,3–0,5 dl/g. According to the data of the dynamic thermogravimetry (air, $\Delta T = 4{,}5\,^\circ C/min$), poly(benzimidazoloquinazoline)s **30**, even those containing ether bonds in the macromolecules revealed a weight loss of 5% at 560 °C or higher and a weight loss of 10% at 580 °C or higher.

The method for synthesizing "step-ladder" polymers described in this article is rather universal. It can be used both in the synthesis of polymers based on diamines containing a 1,2,4-triazole or a benzimidazole ring in *o*-position to one amino group and those based on diamines containing in *o*-position to the amino group indole, pyrrole, pyrimidine or other aromatic nitrogen-containing heterocycles with a reactive hydrogen atom.

Experimental Part

Starting compounds

Diethyl isophthalimidate (**1a**) was prepared by the known method[24] and purified by crystallization from dry ether cooled to –15 to –20 °C. Mp 71 °C; (Lit.[24]: mp 71 °C).

Diethyl terephthalimidate (**1b**) was prepared by the known method[25] and purified by crystallization from dry diethyl ether. Mp 105 °C; (Lit.[25]: mp 102,5–103,5 °C).

Diethyl 2,6-pyridinedicarboximidate dihydrochloride: 12,9 g (0,1 mol) of 2,6-pyridinedicarbonitrile (synthesized by the known method[26]), 250 ml of anhydrous dioxane and 15 ml of dry ethanol were saturated at 0 °C with anhydrous hydrogen chloride for 14–16 h. The reaction mixture was kept at 0 °C for 5 days. The resulting precipitate was filtered, washed with diethyl ether and dried. Mp 110 °C. Yield 87%.

$C_{11}H_{15}N_3O_2Cl\cdot 2HCl$ (329,6)	Calc.	C 44,89	H 5,78	N 14,29	Cl 24,15
	Found	C 44,83	H 5,69	N 14,25	Cl 24,01

Diethyl 2,6-pyridinedicarboximidate (**1c**): The dihydrochloride was dissolved in distilled water at 0 °C, then neutralized with a 30% solution of potassium carbonate. The product was purified by crystallization from dry diethyl ether. Mp 67 °C. Yield 90%.

$C_{11}H_{15}N_3O_2$ (221,3)	Calc.	C 60,00	H 6,78	N 18,99
	Found	C 59,92	H 6,70	N 19,00

o-Nitrobenzhydrazide was synthesized by the known method[27] and purified by crystallization from ethanol; yield 95%; mp 123°C. (Lit.[27]: mp 123°C).

Isophthalamidrazone (**2a**) was synthesized by the known method[28] and crystallized from acetonitrile; the product becomes orange at 150°C and colourless at 280°C, which corresponds to the reported data[28].

Terephthalamidrazone (**2b**) was obtained by the known method[29]; the product has no melting, becomes orange at 180°C and colourless at 300°C, which corresponds to the reported data[29].

2,6-Pyridindicarbamidrazone (**2c**) was produced by the known method[30] and purified by recrystallization from water. Dec.-p. 231°C in a bath, preheated to 210°C. (Lit.[30]: dec.-p. 231°C).

N,N'-Bis(o-nitrobenzoyl)amidrazones (**3a–c**) were obtained by the following procedures: (a) 0,1 mol of the diethyl diimidate (**1a–c**) was boiled with 0,2 mol *o*-nitrobenzhydrazide in 300 ml of ethanol. The yellow product formed during the boiling was filtered off and crystallized.

(b) 0,02 mol of *o*-nitrobenzoic acid chloride was added dropwise at 0°C to the stirred mixture of 0,01 mol of the dicarbamidrazone (**2a–c**), 30 ml of dimethylacetamide, and 2,12 g (0,02 mol) of sodium carbonate. The reaction mixture was stirred for 3 h and poured into ice/water; the resulting yellow products were identical to those synthesized by method (a). The properties and the results of the elemental analyses of the products **3a–c** are given in Tab. 1.

Bis[5-(o-nitrophenyl)-1,2,4-triazole-3-yl]-benzenes or -pyridine (**4a–c**) were obtained by heating of **3a–c** i. vac. (0,5–1 mbar). The conditions of the synthesis, the general characteristica and the results of the elemental analyses of **4a–c** are given in Tab. 1.

Bis[5-(o-aminophenyl)-1,2,4-triazole-3-yl]-benzenes or -pyridine (**5a–c**) were obtained by reduction of **4a–c** with hydrazine-hydrate on Raney-Ni in boiling ethanol for 4–6 h. The general properties of the products are listed in Tab. 1.

2-(o-Aminophenyl)benzimidazole was synthesized by three routes:

(a) *N-(2-Nitrophenyl)-2-nitrobenzamide* was synthesized by the method described earlier[15]. The product was recrystallized from acetic acid; yield 80%; mp 168–169°C; (Lit.[15]: mp 167–168°C). 10 g of *N*-(2-nitrophenyl)-2-nitrobenzamide were dissolved in 100 ml of DMF and placed together with Raney-Ni into the rotating autoclave to accomplish catalytic reduction at 25°C and a hydrogen pressure of ≈101 bar (100 atm). After a pressure decrease to ≈40 bar (40 atm) the reaction mixture was filtered to remove the Raney-Ni, 85 ml of DMF were distilled off on a rotatory evaporator and 200 ml of distilled water were added to the residue. The resulting light-grey product was recrystallized from aqueous methanol to yield *N*-(2-aminophenyl)anthranilamide. Yield 90%; mp 127°C; (Lit.[15]: mp 129–130°C). 5 g of the resulting anthranilamide were placed in a reaction flask and 50 ml of 4 M HCl were added. The mixture was heated under reflux for 2 h. The precipitate was then filtered off, washed with water and treated with aqueous ammonia. The resulting product was sublimated at 150°C (10^{-4} mbar) to give 2-(*o*-aminophenyl)benzimidazole; mp 211–212°C. (Lit.[31]: mp 213–214°C). Yield 70%.

Tab. 1. Conditions for the synthesis, properties and elemental analysis of diamines and some intermediates

Compound	Cyclization temp. in °C (reaction time in h)	Recrystallization from
N^2,N'^2-Bis(*o*-nitrobenzoyl)isophthalamidrazone (**3a**)		DMF
N^2,N'^2-Bis(*o*-nitrobenzoyl)terephthalamidrazone (**3b**)		DMF/water (1:1)
N^2,N'^2-Bis(*o*-nitrobenzoyl)-2,6-pyridinedicarbamidrazone (**3c**)		Ethanol
1,3-Bis[5-(*o*-nitrophenyl)-1,2,4-triazol-3-yl]benzene (**4a**)	260(3)	Ethanol/water (1:1)
1,4-Bis[5-(*o*-nitrophenyl)-1,2,4-triazol-3-yl]benzene (**4b**)	260(3)	Acetone/water (1:1)
2,6-Bis[5-(*o*-nitrophenyl)-1,2,4-triazol-3-yl]pyridine (**4c**)	210(4)	Acetone/water (1:4)
1,3-Bis[5-(*o*-aminophenyl)-1,2,4-triazol-3-yl]benzene (**5a**)		Dioxane/water (1:1)
1,4-Bis[5-(*o*-aminophenyl)-1,2,4-triazol-3-yl]benzene (**5b**)		DMF/water (1:2)
2,6-Bis[5-(*o*-aminophenyl)-1,2,4-triazol-3-yl]pyridine (**5c**)		Ethanol
3,3'Dinitro-4,4'-bis(2-nitrobenzoylamino)biphenyl (**8a**)		DMF
Bis[3-nitro-4-(2-nitrobenzoylamino)phenyl]ether (**8b**)		DMF/H_2O (1:1)
3,3'-Diamino-4,4'-bis(2-aminobenzoylamino)biphenyl (**9a**)		Sublimation
Bis[3-amino-4-(2-aminobenzoylamino)phenyl]ether (**9b**)		Sublimation

(b) 2-(*o*-Aminophenyl)benzimidazole was synthesized by the reaction of *o*-phenylenediamine with anthranilic acid in PPA by the method described earlier[31]. Yield 70%. Mp 212°C. (Lit.[31]: mp 213–214°C).

Tab. 1. Continued

Yield in %	Mp in °C	Brutto Formula	Elemental analysis Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
90	230 dec.	$C_{22}H_{18}N_8O_6$	53,60	3,62	22,54	53,88	3,67	22,83
92	245 dec.	$C_{22}H_{18}N_8O_6$	53,70	3,59	22,48	53,88	3,67	22,83
88	199–200 dec.	$C_{21}H_{17}N_9O_6$	50,98	3,38	25,63	51,40	3,46	25,66
78,5	246–247	$C_{22}H_{14}N_8O_4$	59,33	2,84	24,33	58,15	3,07	24,67
80	313–315	$C_{22}H_{14}N_8O_4$	57,72	2,90	24,65	58,15	3,07	24,67
90	315	$C_{21}H_{13}N_9O_4$	55,15	2,40	27,35	55,40	2,42	27,70
70	318–320	$C_{22}H_{18}N_8$	66,02	4,94	27,90	66,62	4,63	28,35
75	330–331	$C_{22}H_{18}N_8$	66,84	4,52	28,04	66,62	4,63	28,35
70	338–340[a]	$C_{21}H_{17}N_9$	63,45	3,87	31,63	63,81	4,05	31,90
68	365	$C_{26}H_{16}N_6O_{10}$	54,59	2,54	14,61	54,55	2,82	14,68
65	277	$C_{26}H_{16}N_6O_{11}$	52,48	2,62	14,26	53,07	2,74	15,28
50	364–366[b]	$C_{26}H_{20}N_6$	75,16	4,89	20,10	74,98	4,84	20,18
50	295–297[c]	$C_{26}H_{20}N_6O$	72,47	5,04	19,29	72,21	4,66	19,48

[a] Lit.[16]: mp 338 °C. [b] Lit.[17]: mp 372–373 °C. [c] Lit.[17]: mp 296–297 °C.

(c) 4,3 g of *o*-phenylenediamine and 50 ml of DMSO were placed in a flask. The solution was heated to 50 °C and equal amount of *o*-nitrobenzaldehyde was gradually added. Then, the temperature of the reaction mixture was raised to 80 °C and the stirring was continued at this temperature for 6 h. After cooling the reaction mixture was poured into water. The yellow powder-like product was recrystallized from ethanol to give 2-(*o*-nitrophenyl)benzimidazole in 85% yield; mp 266–268 °C; (Lit.[32]: mp 263 °C, yield 80%). 4,4 g of 2-(*o*-nitrophenyl)benzimidazole and 90 ml of ethanol were placed into the reactor and 20 ml of hydrazine hydrate and Raney-Ni were added to the mixture, which was boiled for 5 h with stirring. The Raney-Ni was filtered off from the hot solution and 2-(*o*-aminophenyl)benzimidazole precipitated from the filtrate on cooling; mp 211–212 °C.

Bis[2-(2-aminophenyl)benzimidazole-5-yl]ether (**11b**): 8,7 g of bis(4-amino-3-nitrophenyl)ether **6b** were dissolved in 80 ml of *N*-methylpyrrolidone. 13,2 g of 2-nitrobenzoylchloride were dropped into the solution at 25 °C with vigorous stirring. The mixture was stirred for 20 h and the resulting solution was poured into water to obtain a yellow powder, which was filtered off and recrystallized (Tab. 1). 10 g of the resulting bis[4-(*o*-nitrobenzoylamino)-3-nitrophenyl] ether (**8**) was dissolved in 100 ml of DMF, and the solution was placed into a rotatory autoclave together with Raney-Ni. The catalytic reduction was carried out at 25 °C and an initial hydrogen pressure of ≈ 101 bar (100 atm). When the hydrogen pressure has dropped to ≈ 40 bar (40 atm) after 7 h the reduced product was separated from Raney-Ni and poured into 500 ml of water. The precipitated powder-like product was filtered off, washed with water and boiled with 100 ml of 4 M HCl without additional purification. After 1 h a powder-like product began to precipitate from the resulting solution. It was filtered off and treated with aqueous ammonia. The product was neutralized with water, dried i. vac. at 50 °C (5 mbar) and sublimed at 270–310 °C (10^{-4} to 10^{-3} mbar). Mp 295–297 °C.

2,2′-Bis(2-aminophenyl)-5,5′-bi(benzimidazole) (**11a**) was synthesized from 3,3′-dinitrobenzidine under similar conditions. Mp 364–366 °C.

Aromatic dicarboxylic acid dichlorides **15a–h** were synthesized by known methods[13].

Synthesis of the model compounds

3-Phenyl-5-(o-benzoylaminophenyl)-1,2,4-triazole (**13**) was synthesized by the known method[12] and purified by crystallization from DMF/water (1 : 1). Dec.-p. 256 °C.

3,5-diphenyl-1,2,4-triazolo[4,3-o]quinazoline (**14a**) was obtained:

(a) By the reported method[12] and crystallized from ethanol; mp 175 °C.

(b) By the reaction of 0,01 mol of 5-(*o*-aminophenyl)-3-phenyl-1,2,4-triazole (**12**) with 0,01 mol of benzoic acid in 15 ml of PPA at 50 °C for 1 h, then at 100 °C for 1 h, at 150 °C for 1 h, at 200 °C for 1 h, and finally at 220 °C for 12 h. The synthesized product was sublimed at 250–255 °C (1 mbar) and crystallized from ethanol. Mp 175 °C.

N,N′-Bis[(5-phenyl-1,2,4-triazole-3-yl)phenyl]arylene diamides and derivatives (**16a–h**) were prepared by known methods[13,18]; the general properties, yields, and elemental analyses of the products are given in Tab. 2a–d.

Bis(2-phenyl-1,2,4-triazolo[4,3-c]quinazole-5-yl)derivatives of aromatic hydrocarbons, diarylethers diarylketones, and diarylsulfones (**17a–h**) were prepared by thermal cyclodehydration of **16a–h** their general properties yields, and elemental analyses being represented in Tab. 2a–d.

Tab. 2a. Conditions for the syntheses and properties of *N*,*N'*-bis[(5-phenyl-1,2,4-triazole-3-yl)-phenyl]arylenediamides (**16a–h**)

N,*N'*-Bis[(5-phenyl-1,2,4-triazole-3-yl)phenyl]-	% Yield	Mp in °C	Crystallized in	UV-Spectra[a] λ_{max}/nm	log ε
-isophthalamide (**16a**)	86,3	328–330	DMF/H_2O (2:1)	215/342	4,87/4,13
-terephthalamide (**16b**)	83	380–382	DMF/H_2O (2:1)	285/346	4,78/4,28
-2,6-pyridinedicarboxamide (**16c**)	80	355–358	DMF	262/286/370	4,83/4,89/4,6
-4,4'-biphenyldicarboxamide (**16d**)	78,8	391–394	DMF	279/326	4,89/4,75
-2,6-naphthalinedicarboxamide (**16e**)	81	330	DMF/H_2O (1:2)	256	4,83
-4,4'-oxydibenzamide (**16f**)	75	320	DMF/H_2O (1:1)	239/275	4,35/4,75
-4,4'-carbonyldibenzamide (**16g**)	78	315	DMF	280/340	4,0/4,31
-4,4'-sulfonyldibenzamide (**16h**)	84	308–310	DMF/H_2O (1:1)	285/340	4,9/4,22

[a] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}).

Tab. 2b. Conditions for the syntheses and properties of bis(2-phenyl-1,2,4-triazolo[4,3-*c*]quinazole-5-yl] derivatives of aromatic hydrocarbons, diarylethers, diarylketones, and diarylsulfones (**17a–h**)

Bis[2-phenyl-1,2,4-triazolo[4,3-*c*]quinazole-5-yl]-	% Yield	Mp in °C	Crystallized in[a]	UV-Spectra[b]		Dec.-temp. in °C			Cycliz.-temp. in °C (reaction time in h)
				λ_{max}/nm	log ε	Beginning	Max. I	Max. II	
-benzene (1,3-) (**17a**)	75	333–335	DMF	289/345	5,04/4,5	440	490	560	375–385 (3–4)
-benzene (1,4-) (**17b**)	76	368–370	DMA	289/345	5,02/4,4	440	500	580	375–385 (3–4)
-pyridine (2,6-) (**17c**)	80	356–358	DMF/ ethanol (1:1)	262/288/342	4,87/4,82/4,34	440	500	580	360–375 (4)
-biphenyl (4,4′-) (**17d**)	75	397–400	DMA	278/400	4,75/4,68	460	505	590	390–395 (4)
-naphthalene (2,6-)(**17e**)	82	366–367	DMF	276/370	5,2/4,6	450	500	580	400 (4)
-phenyl ether (**17f**)	80	310	DMA/ ethanol (1:1)	277/400	5,16/4,68	430	510	600	300–320 (4)
-phenyl ketone (**17g**)	85	330–331	DMF	294/351	5,01/4,68	430	510	600	400 (4)
-phenyl sulfone (**17h**)	80	345–348	DMA	289/346	4,94/4,46	460	515	580	330–334 (3–4)

[a] DMA = *N*,*N*-dimethylacetamide. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}).

Tab. 2c. Conditions for the synthesis and properties of bis[5-(*o*-benzoylaminophenyl)-1,2,4-triazole-3-yl]- and bis(5-phenyl-1,2,4-triazolo[4,3-*c*]quinazole-3-yl)-benzenes and -pyridine (**18a–c** and **19a–c**)

Compound	% Yield	Mp in °C	Crystallized in	UV Spectra		Dec.-temp. in °C			Cycliz.-temp. in °C (reaction time in h)
				λ_{max}/nm	log ε	Beginning	Max. I	Max. II	
Bis[5-(*o*-benzoylaminophenyl)-1,2,4-triazole-3-yl]-									
-benzene (1,3-) (**18a**)	85	310	Ethanol	261	4,83				
-benzene (1,4-) (**18b**)	80	382–383	DMF	251/298	4,7/4,8				
-pyridine (2,6-) (**18c**)	75	326	DMF	257	4,8				
Bis(5-phenyl-1,2,4-triazolo[4,3-*c*]quinazole-3-yl)-									
-benzene (1,3-) (**19a**)	76,3	315	Acetone	269/283/352	4,73/4,75/4,87	460	530	600	325–330 (3)
-benzene (1,4-) (**19b**)	65	368–370	DMF/H_2O (1:1)	265/285	4,2/4,3	490	540	610	370 (4)
-pyridine (2,6-) (**19c**)	65	264–264,5[b]	DMF/H_2O (1:1)	261/288/340	4,91/5,0/4,4	430	500	530	350 (4)

[a] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [b] Lit.[6]: mp 264–264,5 °C.

Tab. 2d. Elemental analyses of the model compounds **16a–h, 17a–h, 18a–c**, and **19a–c**

Comp.	General formula	Calc.			Found		
		C	H	N	C	H	N
16a	$C_{36}H_{26}N_8O_2$	71,75	4,35	18,60	71,28	4,44	18,09
16b	$C_{36}H_{26}N_8O_2$	71,75	4,35	18,60	71,16	4,30	18,30
16c	$C_{35}H_{25}N_9O_2$	69,65	4,14	20,90	69,32	4,10	20,58
16d	$C_{42}H_{30}N_8O_2$	74,33	4,42	16,52	74,03	4,49	15,90
16e	$C_{40}H_{28}N_8O_2$	73,60	4,30	17,17	73,70	4;03	16,99
16f	$C_{42}H_{30}N_8O_3$	72,06	4,32	16,16	71,95	4,15	16,02
16g	$C_{43}H_{30}N_8O_3$	73,08	4,24	15,87	72,84	4,18	15,94
16h	$C_{42}H_{30}N_8O_4S$	67,92	4,04	16,00	67,58	4,16	15,89
17a	$C_{36}H_{22}N_8$	76,32	3,89	19,79	75,93	3,82	19,84
17b	$C_{36}H_{22}N_8$	76,32	3,89	19,79	76,03	3,75	19,61
17c	$C_{35}H_{21}N_9$	74,02	3,70	22,22	73,44	4,0	22,22
17d	$C_{42}H_{26}N_8$	78,50	4,06	17,44	77,33	4,15	17,27
17e	$C_{40}H_{24}N_8$	77,92	3,88	18,18	77,49	3,44	17,67
17f	$C_{42}H_{26}N_8O$	73,56	3,95	17,02	72,15	4,17	16,58
17g	$C_{43}H_{26}N_8O$	77,01	3,98	16,71	76,59	3,78	16,82
17h	$C_{42}H_{26}N_8O_2S$	71,10	3,68	15,86	70,92	3,52	15,76
18a	$C_{36}H_{26}N_8O_2$	71,59	4,32	18,70	69,83	4,49	18,70
18b	$C_{36}H_{26}N_8O_2$	71,59	4,32	18,70	71,08	4,38	18,35
18c	$C_{35}H_{25}N_9O_2$	70,82	4,96	21,27	70,47	4,16	21,05
19a	$C_{36}H_{22}N_8$	76,32	3,88	19,80	76,85	3,98	19,18
19b	$C_{36}H_{22}N_8$	76,32	3,88	19,80	76,70	3,40	19,74
19c	$C_{35}H_{21}N_9$	74,07	3,70	22,22	73,92	3,49	21,98

Bis[5-(o-benzoylaminophenyl)-1,2,4-triazole-3-yl]-benzenes or -pyridine (**18a–c**) were synthesized by described methods[13,18], their general properties yields, and elemental analyses are given in Tab. 2a–d.

Bis(5-phenyl-1,2,4-triazolo[4,3-c]quinazole-3-yl)-benzenes or -pyridine **19a–c** were synthesized by the described methods[13,18]; their general properties together with the yields and elemental analyses are given in Tab. 2a–d.

2-(o-Benzoylaminophenyl)benzimidazole (**21**) was prepared by the reaction of equal amounts of 2-(*o*-aminophenyl)benzimidazole (**20**) and benzoyl chloride in freshly distilled dry *N,N*-dimethylacetamide. The product was precipitated by pouring the reaction mixture into water, filtered and recrystallized from ethanol. Yield 90%; mp 252–254 °C (Lit.[33]: mp 251 °C).

N,N'-Bis[2-(benzimidazol-2-yl)phenyl]arylenediamides **23a–h** were prepared by reaction of 2-(*o*-aminophenyl)benzimidazole (**20**) with aromatic dicarboxylic acid dichlorides **15** in dimethylacetamide. The products were separated by pouring the solutions into distilled water. The products were washed with water, ethanol and dried i. vac.

2,2'-Bis(o-benzoylaminophenyl)-5,5'-bi(benzimidazole) (**25a**) *and bis[2-(o-benzoylaminophenyl)benzimidazole-4-yl] ether* (**25b**) were prepared by the reaction of **11a** and **11b**, respectively, with benzoyl chloride in dimethylacetamide. The products were separated by pouring the reaction solutions into water, filtered, washed with water, ethanol and dried i. vac.

6-Phenylbenzimidazolo[1,2-c]quinazoline (**22**) was prepared by heating 2-(2-benzoylaminophenyl)benzimidazole at 250 °C (1 mbar) for 6 h or by the reaction of 2-(2-aminophenyl)benzimidazole (**20**) with benzoic acid in PPA at 210–220 °C for 10 h. The product was purified by recrystallization from ethanol or by sublimation at 220 °C (1 mbar). Yield 90%. Mp 240–241 °C. (Lit.[19]: mp 242 °C).

Bis(benzimidazolo[1,2-c]quinazole-6-yl) derivatives of aromatic hydrocarbons, diarylethers, diarylketones, and diarylsulfones (**24a–h**) were prepared by heating **23a–h** at 300–350 °C (10^{-4} to 10^{-3} mbar). Yields 70–80%. Mp and elemental analyses are given in Tab. 3a, b.

6,6'-Diphenyl-3,3'-bi(benzimidazolo[1,2-c]quinazoline) (**26a**) *and bis(6-phenylbenzimidazolo[1,2-c]quinazole-3-yl) ether* (**26b**) were prepared by heating **25** at 300–350 °C (10^{-4} to 10^{-3} mbar) and purified by sublimation at 350–380 °C (10^{-4} to 10^{-3} mbar), or recrystallization from DMF. Yields: 70–80%. Mp and elemental analyses are given in Tab. 3a, b.

Synthesis of polymers

Poly(triazole-3,5-diylarylenetriazole-3,5-diyl-1,2-phenyleneiminocarbonylarylene carbonylimino-1,2-phenylene (**27a–x**) *and poly(6,2-benzimidazolediyl-1,2-phenyleneiminocarbonylarylenecarbonylimino-1,2-phenylene-2,6-benzimidazolediylarylene)s* (**29**) were synthesized by the following general method: 0,01 mol of the starting diamine and 30 ml of HMPT containing 5% of LiCl were placed in a 50 ml four-necked flask equipped with a mechanical stirrer, a thermometer, an argon inlet, and a funnel for the introduction of aromatic dicarboxylic acid dichlorides. The mixture was stirred until complete dissolution of the diamines was achieved and then equal amounts of the corresponding aromatic

Tab. 3a. Properties of 6-phenylbenzimidazo[1,2-*c*]quinazoline (**22**), its derivatives **26a, b,** and other imidazo[1,2-*c*]quinazoline derivatives **24a–h**

Compound Bis(benzimidazo[1,2-*c*]-quinazole-6-yl)-	Mp in °C	UV Spectra[a)] λ_{max}/nm	 log ε	Dec.-temp. in °C Max. I	 Max. II
-benzene (1,3-) (**24a**)	241–242[b)]	241,5/272	4,36/4,63	455	485
-benzene (1,4-) (**24b**)	332	244/293	4,54/4,92	515	570
-pyridine (2,6-) (**24c**)	415[c)]	243/274	4,61/4,79	520	600
-biphenyl (4,4′-) (**24d**)	355	245/299	4,72/5,08	525	615
-naphthalene (2,6-) (**24e**)	438	243/275	4,56/4,77	520	625
-phenyl ether (**24f**)	472	222,5/243/300	4,93/4,73/4,91	540	620
-phenyl ketone (**24g**)	372	243/293	4,71/4,88	545	615
-phenyl sulfone (**24h**)	370	243,5/296	4,77/5,12	540	625
6-Phenylbenzimidazo[1,2-*c*]-quinazoline (**22**)	405	243,5/294	4,59/4,92	545	610
6,6′-Diphenyl-3,3′-bi(benzimid-azolo[1,2-*c*]quinazoline) (**26a**)	370–380[d)]	250/306	4,68/4,89	550	635
Bis(6-phenylbenzimidazolo[1,2-*c*]-quinazole-3-yl) ether (**26b**)	270–315	246,5/305	4,74/4,91	560	640

[a)] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [b)] Lit.[19,20)]: mp 242 °C. [c)] Lit.[20)]: mp > 350 °C. [d)] Lit.[20)]: mp > 250 °C.

Tab. 3b. Elemental analyses of the model compounds **22**, **24a–h**, and **26a, b**

Comp.	General formula	Calc.			Found		
		C	H	N	C	H	N
24a	$C_{34}H_{20}N_6$	79,68	3,91	16,41	80,09	3,87	16,55
24b	$C_{34}H_{20}N_6$	79,68	3,91	16,41	79,06	3,92	15,98
24c	$C_{33}H_{19}N_7$	77,17	3,73	19,10	77,74	3,84	19,70
24d	$C_{40}H_{24}N_6$	81,61	4,11	14,28	82,08	4,05	14,42
24e	$C_{38}H_{22}N_6$	81,05	4,00	14,95	80,78	3,90	13,92
24f	$C_{40}H_{24}N_6O$	79,44	4,00	13,92	79,67	3,76	13,76
24g	$C_{41}H_{24}H_6O$	79,86	3,92	13,63	79,84	3,86	13,61
24h	$C_{40}H_{24}N_6O_2S$	73,60	3,71	12,88	73,56	3,89	13,10
22	$C_{20}H_{13}N_3$	81,34	4,43	14,23	31,35	4,67	14,22
26a	$C_{40}H_{24}N_6$	81,62	4,11	14,27	80,56	3,86	14,19
26b	$C_{40}H_{24}N_6O$	79,45	4,00	13,89	79,31	4,09	13,79

Tab. 4a. Properties and yields of poly(triazole-3,5-diyl-1,4-phenylenetriazole-3,5-diyl-1,2-phenyleneiminocarbonylarylenecarbonylimino-1,2-phenylene)s (**27a–h**)

Poly(triazole-3,5-diyl-1,4-phenylene-triazole-3,5-diyl-1,2-phenyleneimino-	% Yield	Colour[a]	UV Spectra[b]		η_{sp}/c[c]	Solubility in[d]			
			λ_{max}/nm	log ε	in dl g^{-1}	HMPT	F_3CCO_2H	HCO_2H	H_2SO_4
-isophthaloylimino-1,2-phenylene) (**27a**)	80	l.b.	236/294	4,35/4,48	0,41	s	s	s	s
-terephthaloylimino-1,2-phenylene (**27b**)	75	l.b.	248/296	4,45/4,67	0,52	s	s	s	s
-carbonyl-2,6-pyridinediylcarbonylimino-1,2-phenylene) (**27c**)	82	l.y.	290	4,47	0,6	s	s	s	s
-carbonyl-4,4′-biphenylylenecarbonylimino-1,2-phenylene) (**27d**)	80	l.b.	305	4,65	0,28	ps	s	ps	s
-carbonyl-2,6-naphthylenecarbonylimino-1,2-phenylene) (**27e**)	78	l.y.	256/289	4,8/4,67	0,55	ps	s	ins	s
-carbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonylimino-1,2-phenylene) (**27f**)	85	w.	236/290	4,73/4,72	0,33	ps	s	ins	s
-carbonyl-1,4-phenylenecarbonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27g**)	86	y.	280	4,55	0,27	ps	s	ins	s
-carbonyl-1,4-phenylenesulfonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27h**)	75	l.b.	292	4,55	0,43	ps	s	ins	s

[a] l.b. = light brown; y. = yellow; w. = white. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solutions in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 4b. Properties and yields of poly(triazole-3,5-diyl-1,3-phenylenetriazole-3,5-diyl-1,2-phenyleneiminocarbonylarylenecarbonylimino-1,2-phenylene)s (**27i–p**)

Poly(triazole-3,5-diyl-1,3-phenylene-triazole-3,5-diyl-1,2-phenyleneimino-	Yield	Colour[a]	UV Spectra[b]		η_{sp}/c[c]	Solubility in[d]			
			λ_{max}/nm	log ε	in dl g^{-1}	HMPT	F_3CCO_2H	HCO_2H	H_2SO_4
-isophthaloylimino-1,2-phenylene) (**27i**)	85	l.b.	275/352	4,92/4,45	0,36	s	s	ps	s
-terephthaloylimino-1,2-phenylene) (**27j**)	90	l.b.	282/370	4,96/4,41	0,31	s	s	ps	s
-carbonyl-2,6-pyridinediylcarbonyl-imino-1,2-phenylene) (**27k**)	75	l.y.	275/352	4,76/4,4	0,71	s	s	ps	s
-carbonyl-4,4'-biphenylylenecarbonyl-imino-1,2-phenylene) (**27l**)	80	l.b.	274/390	4,87/4,64	0,41	s	s	ps	s
-carbonyl-2,6-naphthylenecarbonyl-imino-1,2-phenylene) (**27m**)	75	w.	273/368	4,96/4,85	0,6	s	s	ins	s
-carbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonylimino-1,2-phenylene) (**27n**)	82	w.	273/392	4,95/4,36	0,32	s	s	ins	s
-carbonyl-1,4-phenylenecarbonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27o**)	78	y.	383/347	4,96/4,65	0,33	ps	s	ins	s
-carbonyl-1,4-phenylenesulfonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27p**)	80	y.	—	—	0,45	ps	s	ins	s

[a] l.b. = light brown; y. = yellow; w. = white. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solution in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 4c. Properties and yields of poly(triazole-3,5-diyl-2,6-pyridinediyltriazole-3,5-diyl-1,2-phenyleneiminocarbonylarylenecarbonylimino-1,2-phenylene)s (**27q–x**)

Poly(triazole-3,5-diyl-2,6-pyridineyl-triazole-3,5-diyl-1,2-phenyleneimino-	% Yield	Colour[a]	UV Spectra[b] λ_{max}/nm	log ε	η_{sp}/c[c] in dl g^{-1}	Solubility in[d] HMPT	F_3CCO_2H	HCO_2H	H_2SO_4
-isophthaloylimino-1,2-phenylene) (**27q**)	82	w.	282/346	4,95/4,27	0,42	s	s	s	s
-terephthaloylimino-1,2-phenylene) (**27r**)	84	w.	275/355	5,11/4,66	0,35	s	s	s	s
-carbonyl-2,6-pyridinediylcarbonylimino-1,2-phenylene) (**27s**)	78	y.	260/295	4,28/4,18	0,72	s	s	s	s
-carbonyl-4,4′-biphenylenecarbonylimino-1,2-phenylene) (**27t**)	75	y.	260/300	4,84/4,80	0,4	s	s	ps	s
-carbonyl-2,6-naphthylenecarbonylimino-1,2-phenylene) (**27n**)	80	w.	264/310	4,64/4,47	0,45	ps	s	ps	s
-carbonyl-1,4-phenyleneoxy-1,4-phenylenecarbonylimino-1,2-phenylene) (**27v**)	85	y.	273	4,84	0,52	ps	s	ins	s
-carbonyl-1,4-phenylenecarbonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27w**)	78	y.	383/340	4,86/4,34	0,43	ins	s	ins	s
-carbonyl-1,4-phenylenesulfonyl-1,4-phenylenecarbonylimino-1,2-phenylene) (**27x**)	80	y.	272	4,76	0,8	ins	s	ins	s

[a] w. = white; y = yellow. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solution in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 4d. Elemental analyses of the polymers **27a–x**

Substance	General formula	Calc.			Found		
		C	H	N	C	H	N
27a	$C_{30}H_{20}N_8O_2$	68,72	3,81	21,37	87,79	4,65	19,33
27b	$C_{30}H_{20}N_8O_2$	68,72	3,81	21,37	67,74	3,72	19,94
27c	$C_{29}H_{19}N_9O_2$	66,28	3,62	24,06	65,19	4,18	22,55
27d	$C_{36}H_{24}N_8O_2$	72,00	4,0	18,66	69,82	4,55	17,80
27e	$C_{34}H_{24}N_8O_2$	70,83	4,17	19,42	69,93	4,03	18,26
27f	$C_{36}H_{24}N_8O_3$	70,18	3,9	18,18	69,19	3,86	17,63
27g	$C_{37}H_{24}N_8O_3$	70,8	3,81	17,83	69,39	3,92	16,76
27h	$C_{36}H_{24}N_8O_4S$	65,06	3,61	18,87	64,80	4,28	17,05
27i	$C_{30}H_{20}N_8O_2$	68,72	3,81	21,37	67,82	3,72	20,40
27j	$C_{30}H_{20}N_8O_2$	68,72	3,81	21,37	66,85	3,91	19,28
27k	$C_{29}H_{19}N_9O_2$	66,28	3,62	24,06	65,56	4,28	22,83
27l	$C_{36}H_{24}N_8O_2$	72,00	4,0	18,66	70,82	4,29	17,31
27m	$C_{34}H_{24}N_8O_2$	70,83	4,17	19,42	69,17	3,83	19,17
27n	$C_{36}H_{24}N_8O_3$	70,18	3,9	18,18	88,46	4,08	17,69
27o	$C_{37}H_{24}N_8O_4$	70,8	3,81	17,83	71,04	3,83	16,77
27p	$C_{36}H_{24}N_8OS$	65,06	3,61	18,87	63,87	3,61	18,07
27q	$C_{29}H_{19}N_9O_2$	66,30	3,62	24,00	65,98	3,38	22,94
27r	$C_{29}H_{19}N_9O_2$	66,30	3,62	24,00	65,64	3,90	23,07
27s	$C_{28}H_{18}N_{10}O_2$	63,88	3,42	28,61	62,28	3,50	25,96
27t	$C_{35}H_{23}N_9O_2$	70,00	3,82	20,96	68,98	3,75	19,48
27u	$C_{33}H_{23}N_9O_2$	68,63	4,00	21,83	67,84	4,03	21,06
27v	$C_{35}H_{23}N_9O_3$	68,09	3,72	20,42	86,58	3,45	19,17
27w	$C_{36}H_{23}N_9O_3$	68,46	3,64	20,0	67,09	3,70	18,96
27x	$C_{35}H_{23}N_9O_4S$	63,16	3,46	19,0	62,45	3,05	18,20

Tab. 5a. Properties and yields of poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-1,4-phenylene-1,2,4-triazolo[4,3-*c*]quinazoline-3,5-diyl-arylene)s (**28a–h**)

Poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-1,4-phenylene-1,2,4-triazolo-[4,3-*c*]-quinazoline-3,5-diyl-	% Yield	Dec. temp.[a] in °C	UV Spectra[b]		η_{sp}/c in dl g^{-1}	Solubility in[d]		
			λ_{max}/nm	log ε		F_3CCO_2H	HCO_2H	H_2SO_4
-1,3-phenylene) (**28a**)	70	540	293/345	5,04/4,56	0,5–0,45	s	ps	s
-1,4-phenylene) (**28b**)	65	540	296/355	5,48/4,76	0,48–0,45	s	ps	s
-2,6-pyridinediyl) (**28c**)	73	500	290/355	4,96/4,85	0,44–0,2	s	ps	s
-4,4′-biphenylylene) (**28d**)	80	546	289/346	5,04/4,46	0,35–0,3	s	ps	s
-2,6-naphthylene) (**28e**)	70	490	272/368	5,1/4,6	0,53–0,47	s	ins	s
-1,4-phenyleneoxy-1,4-phenylene) (**28f**)	70	460	237/283/404	4,72/5,34/4,35	0,33–0,27	s	ins	s
-1,4-phenylenecarbonyl-1,4-phenylene) (**28g**)	75	470	286/401	4,96/4,33	1,0–1,02	ps	ins	s
-1,4-phenylenesulfonyl-1,4-phenylene) (**28h**)	70	510	292/345	4,95/4,47	0,39–0,51	ps	ins	s

[a] Dec.-temp. = temp. at which a weight loss of 10% is observed at a rate of temp. increase of 4,5 °C/min in air. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solution in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 5b. Properties and yields of poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-1,3-phenylene-1,2,4-triazolo[4,3-*c*]quinazoline-3,5-diyl-arylene)s (**28i–p**)

Poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-1,3-phenylene-1,2,4-triazolo[4,3-*c*]-quinazoline-3,5-diyl-	% Yield	Dec.-temp.[a] in °C	UV Spectra[b] λ_{max}/nm	log ε	η_{sp}/c[c] in dl g^{-1}	Solubility in[d] F_3CCO_2H	HCO_2H	H_2SO_4
-1,3-phenylene) (**28i**)	75	540	277/353	4,75/4,28	0,27-0,25	s	s	s
-1,4-phenylene) (**28j**)	72	540	277/354	5,0/4,4	0,4-0,44	s	s	s
-2,6-pyridinediyl) (**28k**)	68	465	282/342/362	5,02/4,4/4,46	0,72-0,28	s	s	s
-4,4′-biphenylylene) (**28l**)	70	545	264/398	4,96/4,76	0,42-0,47	s	ps	s
-2,6-naphthylene) (**28m**)	70	530	272/313/354	4,75/4,3/4,0	0,5-0,45	s	ins	s
1,4-phenyleneoxy-1,4-phenylene) (**28n**)	65	485	273/394	5,02/4,54	0,54-0,45	s	ins	s
-1,4-phenylenecarbonyl-1,4-phenylene) (**28o**)	70	515	285/348	4,96/4,35	0,4-0,3	s	ins	s
-1,4-phenylenesulfonyl-1,4-phenylene) (**28p**)	70	480	285/355	4,3/4,1	0,4-0,2	s	ins	s

[a] Dec.-temp. = temp. at which a weight loss of 10% is observed at a rate of temp. increase of 4,5 °C/min in air. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solution in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 5c. Properties and yields of poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-2,6-pyridinediyl-1,2,4-triazolo[4,3-*c*]quinazoline-3,5-diylarylene)s (**28q–x**)

Poly(1,2,4-triazolo[4,3-*c*]quinazoline-5,3-diyl-2,6-pyridinediyl-1,2,4-triazolo[4,3-*c*]-quinazoline-3,5-diyl-	% Yield	Dec.-temp.[a] in °C	UV Spectra[b]		η_{sp}/c[c]	Solubility in[d]		
			λ_{max}/nm	log ε	in dl g^{-1}	F_3C O_2H	HCO_2H	H_2SO_4
-1,3-phenylene) (**28q**)	68	495	275	4,16	0,38–0,35	s	s	s
-1,4-phenylene) (**28r**)	70	525	270/340	4,84/4,38	0,56–0,45	s	s	s
-2,6-pyridinediyl) (**28s**)	60	485	283/355	4,98/4,25	0,35	s	ps	s
-4,4′-biphenylylene) (**28t**)	75	520	268/315	5,18/4,68	0,48–0,44	s	ins	s
-2,6-naphthylene) (**28u**)	75	515	266/310	5,14/4,8	0,55–0,47	s	ins	s
-1,4-phenyleneoxy-1,4-phenylene) (**28v**)	72	545	283/347	5,09/4,47	0,6–0,5	s	ins	s
-1,4-phenylenecarbonyl-1,4-phenylene) (**28w**)	65	510	285/350	5,09/4,63	0,45–0,4	s	ins	s
-1,4-phenylenesulfonyl-1,4-phenylene) (**28x**)	65	535	—	—	0,45–0,4	s	ins	s

[a] Dec.-temp. at which a weight loss of 10% is observed at a rate of temp. increase of 4,5 °C/min in air. [b] In H_2SO_4 ($c = 10^{-5}$ mol l^{-1}). [c] 0,5% solution in F_3CCO_2H at 25 °C. [d] s = soluble; ps = partially soluble; ins = insoluble.

Tab. 5d. Elemental analyses of the polymers **28a–x**

Substance	General formula	Calc.			Found		
		C	H	N	C	H	N
28a	$C_{30}H_{16}N_8$	73,77	3,27	22,95	72,46	3,44	22,11
28b	$C_{30}H_{16}N_8$	73,77	3,27	22,95	70,40	3,19	22,33
28c	$C_{29}H_{15}N_9$	71,12	3,65	25,76	69,97	3,45	25,59
28d	$C_{36}H_{20}N_8$	76,60	3,54	20,0	74,93	3,61	19,20
28e	$C_{34}H_{20}N_8$	75,55	3,70	20,74	75,80	3,92	18,47
28f	$C_{36}H_{20}N_8O$	74,48	3,45	19,38	72,99	3,77	18,99
28g	$C_{37}H_{20}N_8O$	74,74	3,36	18,85	73,37	3,72	18,26
28h	$C_{36}H_{20}N_8O_2S$	68,79	3,18	19,42	68,94	3,23	17,96
28i	$C_{30}H_{16}N_8$	73,77	3,27	22,95	69,87	3,98	21,90
28j	$C_{30}H_{16}N_8$	73,77	3,27	22,95	72,27	3,26	21,20
28k	$C_{29}H_{15}N_9$	71,12	3,65	23,76	69,52	3,81	24,98
28l	$C_{36}H_{20}N_8$	76,60	3,54	20,0	74,86	3,68	18,82
28m	$C_{34}H_{20}N_8$	75,55	3,70	20,74	74,77	3,37	20,00
28n	$C_{36}H_{20}N_8O$	74,48	3,45	19,38	72,90	3,46	19,46
28o	$C_{37}H_{20}N_8O$	74,74	3,36	18,85	74,92	3,38	18,86
28p	$C_{36}H_{20}N_8O_2S$	68,79	3,18	19,42	67,04	3,06	18,84
28q	$C_{29}H_{15}N_9$	71,12	3,07	25,76	69,98	3,15	24,89
28r	$C_{29}H_{15}N_9$	71,12	3,07	25,76	68,98	3,24	25,15
28s	$C_{28}H_{14}N_{10}$	68,57	2,85	28,5	66,83	2,75	27,86
28t	$C_{35}H_{19}N_9$	74,34	3,36	22,30	72,98	3,42	21,95
28u	$C_{33}H_{19}N_9$	73,25	3,15	23,29	72,81	3,60	22,05
28v	$C_{35}H_{19}N_9O$	72,30	3,44	21,69	70,85	3,16	20,15
28w	$C_{36}H_{19}N_9O$	72,60	3,25	21,34	71,15	3,02	20,48
28x	$C_{36}H_{19}N_9O_2S$	70,58	3,02	20,03	68,90	2,96	18,35

dicarboxylic acid dichloride were added with vigorous stirring. The reaction was carried out at room temp. for 6–8 h. The resulting reaction mixtures were poured into distilled water and the resulting polymers were thoroughly washed with water until the reaction of Cl^- was negative. Then it was extracted with ethanol for 45–50 h and dried i. vac. at 50–60 °C to a constant weight. The yields, general properties and analyses of **27a–x** are given in Tab. 4a–d.

Poly(1,2,4-triazolo[4,3-c]quinazoline-5,3-diylarylene-1,2,4-triazolo[4,3-c]quinazoline-3,5-diylarylene)s (**28a–x**) *and poly(benzimidazolo[1,2-c]quinazoline-2,6-diylarylenebenzimidazolo[1,2-c]quinazoline-6,2-diylarylene)s* (**30**) were prepared by solid-phase cyclodehydration of **27** and **29**, respectively, i. vac. (pressure 0,5–1,0 mbar) under the following conditions: 50 °C/1 h, 100 °C/1 h, 150 °C/1 h, 200 °C/1 h, 250 °C/1 h, 300 °C/1 h, 350–375 °C/12 h.

The general characteristics, of yields and elemental analyses **28a–x** are listed in Tab. 5a–d.

Synthesis of polymers in PPA: 0,01 mol of the starting diamine, 0,01 mol of an aromatic α,ω-dinitrile and 20 g of PPA were placed in a three-necked flask equipped with a mechanical stirrer and an argon inlet. The mixture was stirred under the following conditions: 100 °C/1 h, 150 °C/1 h, 200 °C/1 h, 250 °C/3 h. The resulting polymers are soluble only in H_2SO_4.

Physical measurements with the polymers and model compounds

Dynamic thermogravimetry and differential thermal analysis were carried ont with a "Paulic, Paulik and Erdey" Derivatograph (Hungary) in air. The temp. increase rate was 4,5 °C/min.

The IR spectra of the model compounds and polymers were taken on IR-10 and IR-20 spectrophotometers with powders pressed with KBr.

The UV spectra of the model compounds and polymers were taken on a "Hitachi" spectrophotometer.

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