



Design of monomeric units for rigid aromatic polymers

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Abstract

The effect of structural inhomogeneities on the equilibrium flexibility of rigid-chain aromatic polymers containing complex condensed cycles in the main chain has been studied. The non-flatness of complex condensed cycles leads to a significant decrease in the equilibrium flexibility of rigid-chain polymers based on them and, consequently, to a deterioration of their mechanical properties. It is shown that the non-planarity of these cycles can reduce the Kuhn segment by several times. The introduction of phenyl substituents into condensed cycles reduces the non-planarity of such cycles and makes it possible to obtain a polymer with sufficiently high physical characteristics.

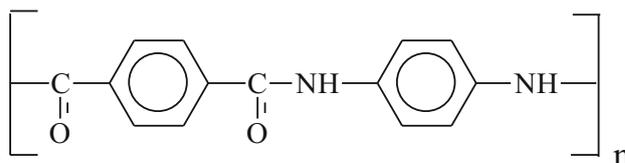
Keywords Complex condensed cycles · Aromatic polymer · Kuhn segment · Non-planarity of cycles

Introduction

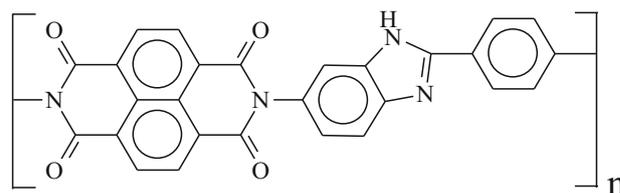
Rigid aromatic hetero-chain and heterocyclic polymers—polyheteroarylenes (PHA) occupy a special place among all types of polymers. Films and fibers based on them have record strength properties and surpass constructional steels and special alloys in the complex of physical and mechanical properties.

There are widely spread fibers: Kevlar® (Du Pont), Terlon® (Russia); fibers ARMOS (Russia) based on poly-*p*-phenylene amidobenzimidazole; completely unique heat-resistant PBZ fibers (USA, Russia) based on poly-*p*-phenylene-bis-benzothiazole (or benzoxazole). In INEOS RAS, together with the ISPM RAS, high-strength IPLON film materials have been developed, based on polynaphthoylenimidobenzimidazole (PNIB), which are 8–10 times better than structural steels in specific strength [1].

All types of polymers listed above contain in the main chain *p*-phenylene fragments connected by hetero bonds, for example, amide in PPhTA



$A_{\text{exp}} = 450 \text{ \AA}$, $A_{\text{fr}} = 1000 \text{ \AA}$ or heterocyclics as in PNIB



$A_{\text{fr}} = 280\text{--}323 \text{ \AA}$

Many researchers have noted that in each class of PHA, the strength properties of films and film-based fibers are the more higher (all other things being equal), the more *p*-phenylene fragment content in the main polymer chain and the higher

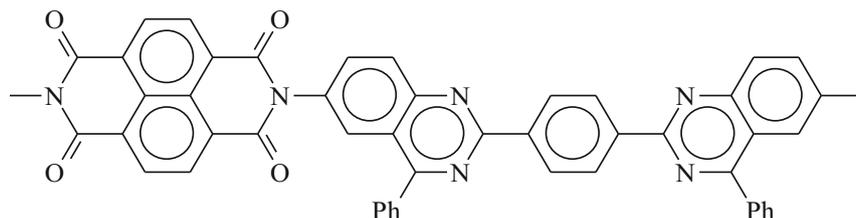
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the Kuhn segment (A_{fr}) is characterizing the equilibrium rigidity of the polymer chain [2].

The value of the Kuhn segment can be measured experimentally and obtained by calculation. Thus, poly(naphthoileimidoquinazoline) (PNIQ), synthesized

in the laboratory of the GTP INEOS of the Russian Academy of Sciences, is soluble in organic solvents



According to the chemical structure, PNIQ should have a Kuhn segment $A_{fr} = \infty$ (since this is a rigid rod that is unable to fold into a coil), while the experimental value of the rigidity of this polymer appeared to be the finite value [3, 4]. Later [5, 6], it was shown that the final stiffness in rodlike poly(naphthoileimide)s (PNI) is probably due to the conformational flexibility of naphthoileimide cycles which equiprobably take conformation of a “chair” or a “boat,” and the main contributing factor to the increase in flexibility being the “boat” form conformation.

In addition to the conformational flexibility of the central heterocycle, the values of the Kuhn segment are affected by the incomplete cyclization of the aromatic heterocycle and the possible isomeric composition of this heterocycle in the chain [7].

Methods of calculation

Calculation of conformational parameters

As it is known, the adequate measure of conformational rigidity is the value of the statistical Kuhn segment. Statistical Kuhn segment A_{fr} was calculated under the assumption of free rotation with Eq. (2) [8]:

$$A_{fr} = \lim_{n \rightarrow \infty} \left(\frac{\langle R^2 \rangle}{nl_0} \right) \quad (1)$$

where $\langle R^2 \rangle / nl_0$ is the ratio of root-mean-square value of end-to-end distance of a chain to its contour length ($L = nl_0$ is a parameter independent of the chain conformation); n is the number of repeating units; and l_0 is the contour length of a repeating unit. In the case of polyheteroarylenes in which the macromolecular unit contains virtual bonds with different lengths and different angles between them, the length of the zig-zag line connecting the mid-points of the virtual bonds is taken as the contour length. The Kuhn segment length was

calculated by the Monte Carlo method. We used Volkenstein rotational isomeric state approximation by consideration of only discrete values of rotation angles, and the Flory approximation by the assumption that rotations around virtual bonds are independent. The term “virtual bonds” is used to indicate a rigid section of a chain approximated by a straight line about which rotation is possible. In a particular case, it can be an ordinary valence bond; more generally, it can contain rings, as well. The conformational energy maps for several aromatic polyesters and polycarbonates were calculated and the minimum energy structures were found, in which the rotation angles about virtual bonds passing through aromatic rings were 0° and 180° , both values being equally probable. This means that these virtual bonds behave as statistically free rotating bonds. With these assumptions one can write coordinates of any vector in the reference frame associated with the first vector as:

$$V_j = T_1 \dots T_{j-2} T_{j-1} l_j$$

where T is the Flory matrix.

$$T_j = \begin{bmatrix} \cos\theta_j & \dots & \dots & \sin\theta_j & \dots & \dots & 0 \\ \sin\theta_j \cos\phi_j & \dots & \dots & -\cos\theta_j \cos\phi_j & \dots & \dots & \sin\phi_j \\ \sin\theta_j \sin\phi_j & \dots & \dots & -\cos\theta_j \sin\phi_j & \dots & \dots & -\cos\phi_j \end{bmatrix} \quad (2)$$

and $(\pi - \theta_j)$ are the angles between virtual bonds. On constructing the polymer chain, the angles θ_j recur periodically with the period depending on the number of virtual bonds N in the repeat structural unit. The index j runs from 1 to $n \cdot N$.

The values of the rotation angles, ϕ_j were chosen in one of the following two ways depending on the nature of the bond: (i) they were determined by the Monte Carlo procedure on the assumption of a uniform distribution within the interval $(0, 2\pi)$; (ii), ϕ was constant, i.e., any rotation about a bond was forbidden. The ensemble average $\langle R^2 / nN \rangle$ was obtained by generating on a computer a set of independent chain sequences (in each sequence n runs from 1 to 2500) and

averaging over the set of R^2/nN values relating to the same n . For each of the polymers, the value of $n = n'$ beyond which the average $\langle R^2/nN \rangle$ as a function of n tended to converge was found. Usually, n' was found to be of the order of 1000 [8].

In [2], it was shown that the value of the Kuhn segment calculated under the assumption of free rotation in the absence of bulk side substituents is approximately equal to the value of the Kuhn segment, found experimentally from hydrodynamic data. This allowed us in a large number of cases when comparing the conformational rigidity with the physical properties of polyheteroarylenes to replace the experimental value of the Kuhn segment by the calculated value under the assumption of free rotation. Moreover, the experimental determination of the of the Kuhn segment value is very laborious and not always unambiguous [2].

Let us consider how the structural heterogeneity influence the value of the Kuhn segment:

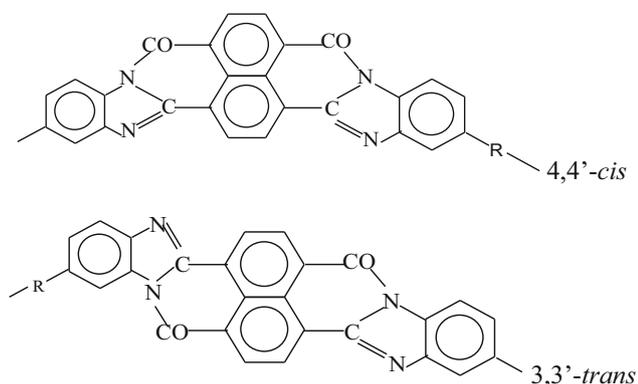
1. Isomeric composition

As an example of the influence of the isomeric composition on the conformational rigidity, we consider polymers polynaphthoylebenzimidazoles (PNBI) (Scheme 1).

Organic fibers based on these polymers possess physical and mechanical characteristics typical for conventional flexible chain polymers (tensile strength of 20–45 cN/tex, an elastic modulus of 10–20 GPa) [9, 10].

Since the formation of several isomeric structures is possible during the synthesis, some of the isomers should have a sufficiently high flexibility. The hydrodynamic, diffusion, and dynamo-optical properties of PNBI ($R = -O-$; $-$) were previously investigated [11–16]

In [17, 18], an X-ray structural study of the structure of model compounds fragmentarily included in PNBI was carried out. It was shown that the *trans* isomer is practically flat and the lengths of bonds and angles are given. The *cis* isomer is less flat, the deviation from the



where $R = -$ (polymer 1); $-O-$ (polymer 2).

Scheme 1. Polynaphthoylebenzimidazoles

middle plane reaches 0.4 Å. These data (bond lengths and angles) were used in the conformational analysis of PNBI macromolecules. Another type of isomerism is characteristic for PNBI. This is a different entry in the polymer chain. Each isomer was built in a molecular editor and refined by the AM1 quantum-chemical method [19]. Table 1 shows six possible isomers, the contour length and calculated for polymers with $R = -$ and $-O-$ Kuhn segment values.

Confirmation parameters of isomers were calculated using the Monte-Carlo method according to the method given in [8]. It should be noted that the use of X-ray data made it possible to clarify the geometric structure of the PNBI unit, which had little effect on the length of virtual bonds, but significantly on the angles between them. In the calculations, it was assumed that the rotation freely around the bonds connecting the cycle with oxygen in polymer 2 and the bonds directly connecting the cycles in polymer 1. In both polymers, the conformation around a virtual bond passing through the naphthoylebenzimidazole cycle in isomers 1, 2, 6 was *trans*, prohibited rotation around it, and in isomers 3-, 4-, 5-*cis*, also with rotation prohibition.

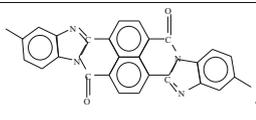
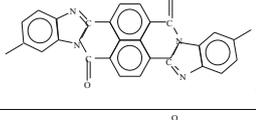
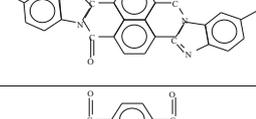
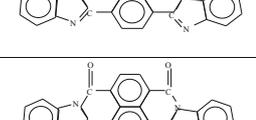
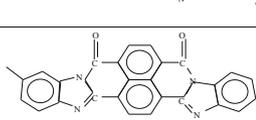
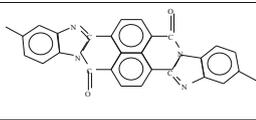
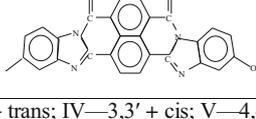
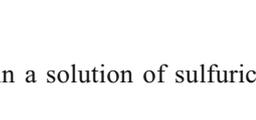
In [12], Kuhn segments were calculated for all PNBI isomers. But in the calculations, we used data on the structure of simple organic compounds that are partly included in the naphthoylebenzimidazole cycle. The results are somewhat different from the data in Table 1, for the most rigid isomers (for example, for isomer 6, of polymer 1 Kuhn segment was 1400 Å [12]). From the Table 1 data, it is clearly seen that the conformational rigidity of polymers based on PNBI isomers varies in a wide range of values, especially for polymer 1.

It was previously established that during the synthesis of PNBI in a polyphosphoric acid medium, macromolecules are formed with an equal content of all isomers [17]. Macromolecules of the compositions *cis/trans* = 0.45/0.55 and 4.4'/3.3' = 0.87/0.13 are formed in the medium of phenol. A two-stage synthesis through the prepolymer stage in the N-methylpyrrolidone solution can produce an almost quantitative content of the 4.4'-isomer with a *cis/trans* ratio of 0.42/0.58. Thus, polycondensation carrying out in various media can change the isomeric composition of polymers in the direction of a higher or lower content of isomers with higher values of the Kuhn segment.

When calculating the Kuhn segment by the Monte Carlo method with equal participation of all six isomers, the value obtained is 81.2 Å.

Table 2 shows the theoretical values of the Kuhn segment and the experimental values found using the characteristic viscosities and molecular masses obtained by the method of translational diffusion in [11–16]. At the same time, the model of a chain of finite length in the Bogdanetsky variant [20] was considered as a model of

Table 1 Possible isomers for PNBI and their conformational parameters

No	Structural repeat unit	$l_o, \text{\AA}$	$A_{fr}, \text{\AA}$
1	 4,4' + <i>trans</i>	16.42	∞
2	 3,3' + <i>trans</i>	16.00	∞
3	 3,4' + <i>trans</i>	15.88	61.3
4	 3,3' + <i>cis</i>	16.73	45.6
5	 4,4' + <i>cis</i>	16.11	99.0
6	 3,4' + <i>cis</i>	15.92	1125
	 I	I 17.41	96.0
		II 16.69	77.2
		III 16.92	27.4
	 IV	IV 16.71	27.8
		V 17.09	36.7
		VI 17.02	151.3

I—4,4' + *trans*; II—3,3' + *trans*; III—3,4' + *trans*; IV—3,3' + *cis*; V—4,4' + *cis*; VI—3,4' + *cis*

the behavior of a macromolecule in a solution of sulfuric acid.

The data given in Tables 1 and 2 show that, despite the existence of highly rigid structures in the mixture of PNBI isomers, the experimentally obtained polymers are not rigidly chained. As shown in [21], the entry into the polymer chain of a rigid chain polymer by even 10% percent of a flexible chain polymer reduces its equilibrium rigidity at times. This, apparently, is connected with

the fact that, contrary to expectations, high-modulus and high-strength films and fibers, as well as crystalline structures [9, 10] were not obtained on the basis of PNBI.

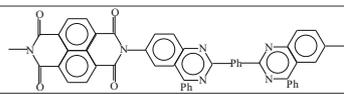
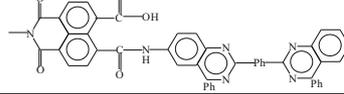
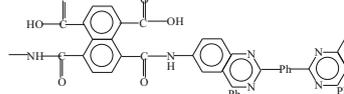
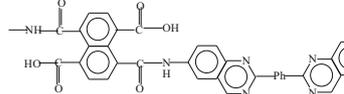
2. Incomplete of cyclization

The behavior of polynaphthoyleneimidoquinazoline (PNIQ) the macromolecules in a diluted solution was studied

Table 2 The theoretical (A_{fr}) and experimental (A_{exp}) value of Kuhn segment for PNBI polymer.

Synthesis medium	Ratio of isomers		$A_{fr}, \text{\AA}$		$A_{exp}, \text{\AA}$	
	4,4'/3,3'	<i>Cis/trans</i>	Polymer 1	Polymer II	Polymer 1	Polymer II
PPhA	0.5/0.5	0/5/0.5	81.2	46.3	96.8	40.0
Phenol	0.87/0.13	0.45/0.55	108.6	53.5	119.0	50.0
N-MP (cyclization in phenol)	1.0/0.0	0.42/0.58	-	57.2	-	50.0

Table 3 Conformational parameters of polymer PNIQ and its derivatives with incomplete cyclization of the naphthoyleimide cycle.

Polymer	Monomer unit	l_0^* , Å	A_{fr} , Å
1		25.34	∞
2		25.87	2231
3		25.61	1406
4		26.65	1317

* l_0 is the contour length of a repeating unit

* l_0 is the contour length of a repeating unit

by the methods of diffusion and birefringence in the flow. The experimental Kuhn segment values determined by these methods are 1200 ± 300 Å [3] and 1600 ± 400 Å [4]. The Kuhn segment was calculated by the Monte Carlo method [16] assuming free rotation. The geometric structure of the PNIQ link was constructed on the basis of X-ray diffraction data of model compounds, [22, 23] and refined by the AM1 method [19]. The value of the Kuhn segment turned out to be ∞ .

This means that the polymer is a rigid rod. This is possible only when all units in the chain are free from defects. However, A_{fr} is the lower limit of A_{exp} . For most polyheteroarylenes, there is an approximate equality between the experimental and theoretical values of the Kuhn segment [8]. Based on this, it can be assumed that there must be defects in the polymer.

Previously, it was assumed that the rigidity of the PNIQ has a finite value due to the deformation of the bonds and angles caused by thermal vibrations [12, 15]. However, it was shown in [24] that thermal oscillations cannot produce such significant changes in the length of bonds and angles. In the case of PNIQ, when the chain consists of σ -linked heterocycles, the effect of thermal oscillations cannot all the more noticeably effect the length of the Kuhn segment. It was then suggested that the reason of the discrepancy between the experimental and theoretical values of the Kuhn segment lies in the incomplete cyclization of the naphthoyleimide cycle.

Table 3 shows the formulas of PNIQ derivatives (polymers 2–4) containing three types of incompletely cyclized naphthoyleimide units. The Kuhn segments calculated for these polymers were rather high. Moreover, it is well known that in the process of synthesis of poly(naphthoyleimide)s in general and PNIQ, in particular, fragments with incomplete cyclization are practically not rested in the final product due to the ease of formation of a six-membered imide cycle [25].

Therefore, the assumption of incomplete cyclization poorly agreed with experimental data.

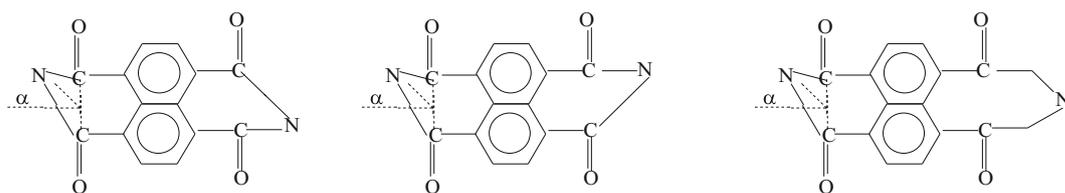
Another assumption is based on the fact that the cause of the final stiffness of the molecules of the PNIQ may be the nonplanarity of the naphthoyleimide cycle.

The nonplanarity of the heterocycle

It is known that cycles containing an imide fragment can easily change their configuration without a significant increase in energy, especially in the case of a naphthoyleimic nucleus, when conjugation with imide fragments of the molecule is not as strongly pronounced as in the pyromelitimide cycle between the phenylene ring and imide cycles [26]. Naphthalene bicycle itself is a tough, hard, and deformable fragment. The carbon atoms of the carbonyl groups are rigidly fixed in the plane of the aromatic rings, as evidenced by X-ray diffraction data [27] and quantum-chemical calculations [28]. Thus, the possible non-planar conformations of the naphthoyleimide cycle can be the “chair,” “boat,” and “half-chair” conformations, which occur due to the release of nitrogen atoms from the cycle plane.

Table 4 Changes in energy during bending of naphthoyleimide cycles

α , °	ΔE , kJ/mol		
	Boat	Chair	Half-chair
5	0.54	0.84	0.25
10	1.80	1.80	0.88
15	3.97	3.87	2.01
29	6.94	7.15	3.47

«cheat», *trans*-conformation«boat», *cis*-conformation «half-cheat», *cis*-conformation**Scheme 2** Three conformations of the naphthoylenimide fragment

In [5], the ability of an imide cycle in a PNIQ molecule to move from a flat equilibrium conformation to a non-planar conformation is shown. Calculations were carried out by semi-empirical quantum-chemical method AM1 [19]. The conformational flexibility of naphthoylenimide cycles was studied by scanning the torsion angle $C_{ar}-C(=O)-N-C(=O)-C_{ar}$, α , in the interval of angles of $\pm 20^\circ$ with 5° increments and the optimization of the other geometric parameters of the molecule. The results of the calculations are given in Table 4. The change of the above torsion angles in the naphthoylenimide cycle can, depending on their sign, lead to the following three conformations of the naphthoylenimide fragment of the molecule (Scheme 2):

From the Table 4 data, it can be seen that the energy required for the transition of the naphthoylenimide ring from the flat conformation to the “boat”, “chair,” and “half-chair” conformations are small. Therefore, a significant content of non-flat conformers in the PNI chain can be expected.

Assuming that the chain consists of conformers of the same kind, the Kuhn segment lengths were calculated for different values α of the angle. As expected, the polymer consisting of fragments in the “armchair” conformation, for all values of the angle α , has a Kuhn segment length equal to ∞ , the same as in the case of a flat heterocycle. For polymers based on fragments in conformations “boat” or “half-chair,” A_{fr} has a finite value already at $\alpha = 5^\circ$. However, for the conformation, the “half-chair” A_{fr} decreases with an α angle increase slower than that for the conformation “boat” (Table 5).

The determination of A_{exp} was carried out under severe conditions (concentrated sulfuric acid) and its accuracy was low [3, 4]. Therefore, we did not seek to determine the exact conformational composition of the polymer. The task was to

show that the presence in the polymer chain of non-planar cycles turns it from a rigid rod into a macromolecule with finite Kuhn segment lengths.

For this, PNIQ was considered as a copolymer consisting of three types of units: units containing a flat naphthoylenimide cycle and units in which this cycle is in the “boat” or in the “chair” conformation. The conformer “half-chair” was not considered in this case, since it is less sensitive to changes in α angle and at the same time is a transition between the “boat” and “chair” conformers. Since nothing indicates anharmonicity of transitions from the “boat” conformation to the “chair” conformation, we supposed that both conformations would be present in the polymer equally probable. When constructing a copolymer, the probability of the inclusion of one or another unit in the chain of the copolymer was taken to be equal to its molar fraction [21]. In Table 6 are shown the values of A_{fr} at different content of units in the “boat” conformation and different values of α —the angle of exit of the nitrogen atom from the plane of the naphthoylenimide ring. The closest to the experimentally found values of the Kuhn segment length are such variants in which the links in conformation “boat” are present in an amount of 10–15% at $\alpha = 20^\circ$ or 15–20% at $\alpha = 15^\circ$.

In fact, in a real polymer, there is a set of conformers with the full range of angles for the emergence of nitrogen atoms from the plane of the naphthoylenimide ring, in the range from 0° to angles slightly exceeding 20° . As already mentioned above, we did not perform an accurate analysis of the distribution of conformers by angles α due to the low accuracy of the experimental determination of the rigidity of this polymer:

Table 5 Calculated values of A_{fr} for PNIQ chains consisting of one kind of conformers.

Conformer	$A_{fr}, \text{Å}$			
	$\alpha = 5^\circ$	$\alpha = 10^\circ$	$\alpha = 15^\circ$	$\alpha = 20^\circ$
Boat	1940	701	332	190.4
Chair	∞	∞	∞	∞
Half-chair	3301	1913	1120	695

Table 6 Calculated values of the Kuhn segment of PNIQ polymer in the presence of non-planar the naphthoylenimide cycle conformations

Content of boat con-former, %	$A_{fr}, \text{Å}$			
	$\alpha = 5^\circ$	$\alpha = 10^\circ$	$\alpha = 15^\circ$	$\alpha = 20^\circ$
5	4310	4040	3925	3531
10	3666	2920	2563	2231
15	2940	2060	1621	1255
20	2200	1424	1069	820

In the chain with equal fractions of “boat” and “chair” conformers

Apparently, during the synthesis of PNIQ as a result of Brownian collisions, the energy necessary for the transition of the naphthoylenimide cycle from the flat conformation to the “boat”, “chair,” or “half-chair” conformations accumulates. In this case, the less such energy, the smaller the angle of escape of nitrogen atoms from the plane of the cycle. When a naphthoylenimide cycle enters the polymer chain, this conformation is frozen, since transitions of the naphthoylenimide cycle to a flat conformation in the polymer chain require much more energy.

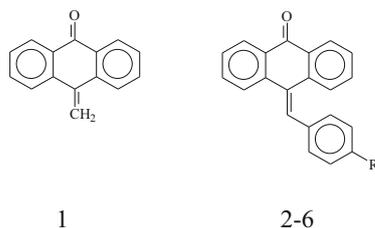
Thus, using PNIQ examples, we analyzed the reasons why real rod-like polynaphthoylenimides possess finite conformational rigidity.

Another example of a possible non-planar conformation is the six-membered cycle in the *n*-quinone. Despite the flat equilibrium conformation, it is highly flexible [29, 30]. When one of the carbonyl groups is replaced by a methylene, the partially hydrogenated ring adopts a “boat” conformation [31]. Thus, the equilibrium conformation of the six-membered cycle in anthroneylidens is nonplanar and at the same time the dihydrocycle must have a high conformational flexibility. This makes these systems very convenient objects for studying the effect of a change in the conformation of the central heterocycle of the monomeric unit on the size of the Kuhn segment of the macromolecule.

In the study of the conformational behavior of the central quinone dihydrocycle in antronylidene compounds (type 1), the task was to determine the effect of various groups in the exocyclic C=C bond on conformational flexibility and equilibrium conformation of molecules 1–6. The selected *R* substituents showed different properties: from strongly electron-donor (NMe₂) to strongly electron-acceptor (NO₂) (Scheme 3).

The spatial structure of compounds 1–6 is optimized by the AM1 semi-empirical quantum-chemical method [19], and when studying their conformational behavior, the torsion angle C_{ar}–C_{ar}–C(=C)–C_{ar} (φ) was varied in the interval of $\pm 40^\circ$ with 10° increments and other geometric parameters were optimized at each increment (Fig. 1). To describe the change in the dihydrocycle geometry, four distances and four angles are necessary (see Scheme 4).

Molecular structures of compounds 2–6 were previously established by X-ray structural analysis [32]. Comparison of



where 2: **R=H**, 3: **R=NMe₂**, 4: **R=OMe**, 5: **R=Cl**, 6: **R=NO₂**.

Scheme 3 Different properties of the selected *R* substituents

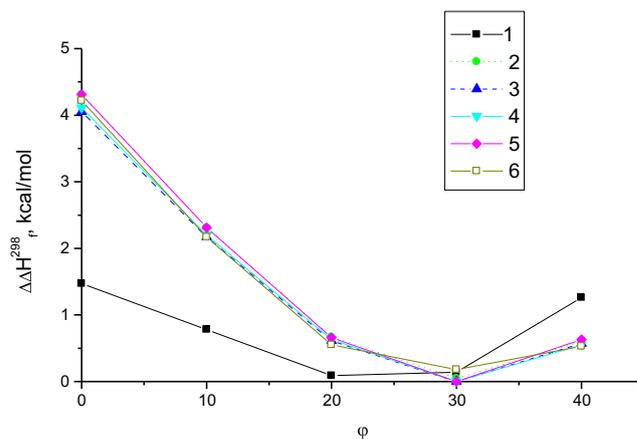
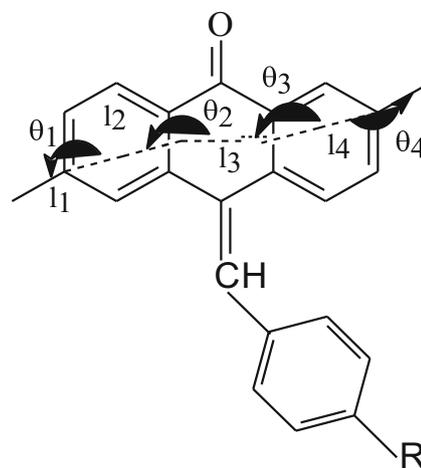


Fig. 1 Dependence of the relative heat of formation of molecules 1–6 on the angle of bending of the dihydrocycle

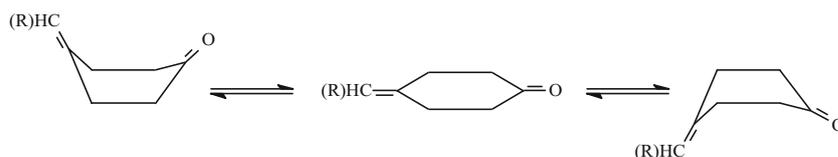
X-ray data with data obtained for these molecules by the AM1 method showed good agreement between the main bond lengths and angles, which justifies the use of this method for such molecular systems. Both methods show that in derivatives 2–6, due to unfavorable non-valence interactions between the *p*-R-C₆H₄ substituent and *per*-H atoms, there is a significant rotation of the benzene ring relative to the C=C bond (the corresponding torsion angles are 2–6~50°), and also its twisting (torsion angles φ 2–6~10°). As a result, the electronic effects of the substituent *R* cannot have a significant effect on the structure of the central antronylidene fragment.

The quinone dihydrocycle in all molecules has an equilibrium conformation of the asymmetric “boat” in agreement with the theoretical [31, 32] and experimental data [32, 33]. Thus, the quinone dihydrocycle in antronylidene compounds can take two equivalent equilibrium conformations, connected by a mirror-rotating reflection plane and passing into each other when overcoming the potential barrier corresponding to the planar conformation of the dihydrocycle (see Scheme 5).

It is known that, for polyheteroarylenes, the value of the Kuhn segment (a measure of the thermodynamic rigidity of



Scheme 4 The change in the dihydrocycle geometry

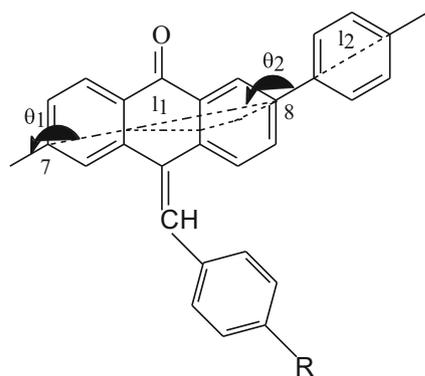
Scheme 5 Equilibrium conformations

the polymer chain) A_{fr} is very sensitive to the geometric structure of a repeating structural unit of the chain [8]. Therefore, it is possible to use the Kuhn segment as a measure of the flexibility of the dihydrocycle to determine which of the substituents R has the greatest effect on the decomposition of the dihydrocycle. [34]. For this purpose, polymers were selected, the structural unit of which contained one constant fragment (*para*-phenylene) and one variable fragment (anthronylidene), with different substituents. Then, the rigidity of the polymer is entirely determined by changes in the structure of the latter. Moreover, the smaller the Kuhn segment is, the more flexible is the polymer and, consequently, the more deformed the dihydrocycle.

Since the conformation of the dihydrocycle is a distorted bath, the geometry of the polymer unit can be described using 2 virtual bonds (l_1, l_2) and 2 angles between them (θ_1, θ_2) (see Scheme 6). Figure 2 shows the dependences of the relative formation heats of molecules 1–6 with a curved quinone dihydrocycle (different values of φ) on the rigidity of the polymer corresponding to it ($\Delta\Delta H_f^{298}$ (A_{fr})). For all compounds, the dependences are nonlinear, but they can be divided into three groups, with respect to the substituents:

- PhCl, PhOMe and PhN(Me)₂
- Ph and PhNO₂
- Polymer based on compound 1

In each of these groups, the values of A_{fr} for angles φ , larger than those in equilibrium structures fit almost on straight lines. The dependences corresponding to group (b) have the greatest slope. This means that with the introduction of these substituents, the partially hydrogenated cycle is more stringent and more energy is required to flatten it. In this case,

**Scheme 6** The geometry of the polymer unit

the heterocycle does not become completely flat, and the rigidity of the corresponding polymer does not reach a maximum.

The Kuhn A_{fr} segment varies in a narrow range: from 85 to 105 Å (Table 7). In molecule 1, the dihydrocycle is the most labile. To flatten this cycle, only 1 kcal/mol is sufficient, and therefore the polymers containing it are the hardest (A_{fr} reaches maximum values ~ 117 Å).

In the calculations described above, each polymer consisted of monomeric units with the same angle of bending of the dihydrocycle. However, in the real polymer, there are links with different torsion angles φ . For a polymer, the dependence of energy on angle φ is the same as for a separate quinone dihydrocycle, due to the large distances between the heterocycles, which allows one to neglect their influence on each other.

Using of this, one can calculate the Kuhn segment of a real polymer, assuming it consists of comonomers with different values of the torsion angle φ , the probability of each of which is determined by the dependence $\Delta\Delta H_f^{293}(\varphi)$. In our case, the polymer is made of six comonomers: five with bending angles in the range from 0 to 40° with an interval of 10° and one with a dihydrocycle in an equilibrium state.

Earlier, a method was developed for calculating the Kuna segment of a copolymer of two comonomers with the probability of each participating in proportion to its molar fraction in the copolymer [21]. For calculations of copolymers containing a greater number of different comonomers, we used the Kuhn segment calculation method in two versions: (a) with the equally probable participation of each of the comonomers

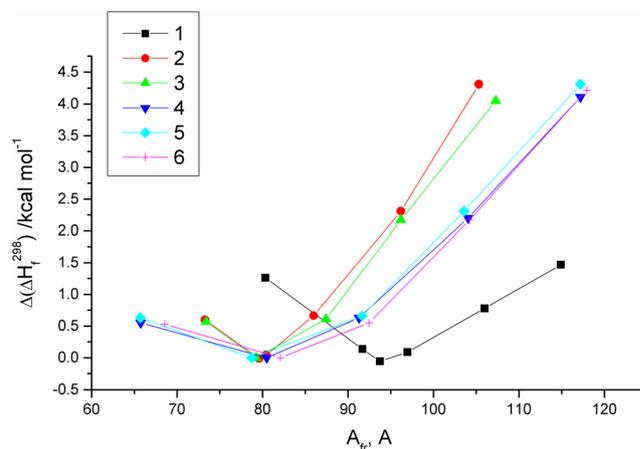
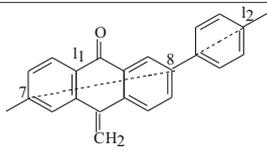
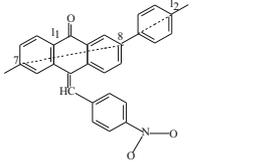
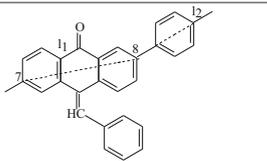
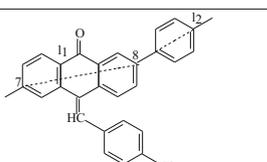
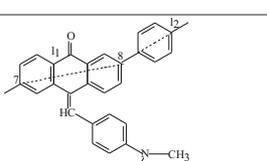
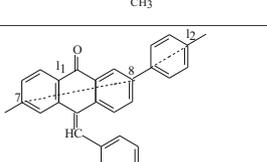
**Fig. 2.** Dependence of the relative formation heat of molecules 1–6 $\Delta\Delta H_f^{293}$ on the value of the Kuhn A_{fr} segment

Table 7 The energy and structural parameters of polymers based on anthroneylidene molecules 1–6

N	Repeat unit	φ , grad	$\Delta\Delta H_f^{293}$, Kcal/mol ⁻¹	A_{fr} , Å	A_{eq} , Å	A_{bolz} , Å
1		0	1.47	114.89	95.44	96.54
		10	0.78	105.98		
		20	0.09	96.97		
		30	0.14	89.02		
		40	1.26	80.33		
		24.7 eq*	0	85.10		
2		0	4.31	105.31	88.42	73.28
		10	2.31	96.20		
		20	0.67	87.42		
		30	0.05	79.18		
		40	0.6	73.27		
		30.6 eq	0	79.00		
3		0	4.0	107.29	79.81	73.42
		10	2.2	96.20		
		20	0.6	87.42		
		30	0	79.24		
		40	0.6	73.40		
		30.0 eq	0	79.26		
4		0	4.1	117.20	91.92	84.62
		10	2.2	104.06		
		20	0.6	91.28		
		30	0	80.47		
		40	0.5	65.74		
		30.1 eq	0	78.49		
5		0	4.3	117.33	89.87	82.28
		10	2.3	103.59		
		20	0.7	91.67		
		30	0	78.74		
		40	0.6	65.72		
		30.4 eq	0	76.64		
6		0	4.3	117.95	90.66	83.57
		10	2.2	104.23		
		20	0.6	92.46		
		30	0.2	82.09		
		40	0.5	68.56		
		30.5 eq	0	75.80		
		28.6 xray	-	82.80		

*The equilibrium structure;** Data of X-ray study

*The equilibrium structure;**data of X-ray study

(A_{eq}); (b) with the probability of the participation of each of the comonomers, determined by the Boltzmann factor [35–37] (A_{bolz}).

Let us consider the second option in more detail. The probability of participation of each type of comonomer (p) is proportional to the energy required to bend the dihydrocycle to the angle corresponding to this comonomer. To calculate this probability, the dependence $\Delta\Delta H_f^{298}(\varphi)$ was interpolated through 1.25° and was used in the determination.

$$p(\varphi) = \exp\left(-\frac{\Delta H_f^{298}(\varphi)}{kT}\right) / Z \quad (3)$$

where the Boltzmann factor

$$Z = \sum_{\varphi} \exp\left(\frac{\Delta H_f^{298}(\varphi)}{kT}\right) \quad (4)$$

The $p(\varphi)$ curve was divided into five sections (according to the number of considered torsion angles of the dihydrocycle): 0–5° interval for the comonomer with $\varphi = 0^\circ$; 5–15°—with $\varphi = 10^\circ$; 15–25°—with $\varphi = 20^\circ$; 25–35°—with $\varphi = 30^\circ$; 35–40°—with $\varphi = 40^\circ$. Angles from 0 to 40° were converted to radians and normalized to a maximum value (ξ varies from 0 to 1). Then the $p(\varphi)$ curve was integrated:

$$p'(\xi) = \int_0^1 p(\xi) d\xi \quad (5)$$

Figure 3 shows the dependence $p'(\xi)$, with the intervals on the abscissa corresponding to the indicated intervals for comonomers with given angles of dihydrocycle bending with equal probable participation of comonomers in the copolymer chain, and along the ordinate axis the same intervals taking into account the Boltzmann factor. Since the axes are normalized to 1, we can consider these intervals as uniform distributions of random numbers between 0 and 1. As can be seen from Fig. 3, the lower the dihydrocycle bending energy, the higher the probability of comonomer occurrence with such a cycle in the polymer and the wider the interval of random numbers for this comonomer and vice versa

To build a polymer chain, a uniformly distributed random number was generated in the range from 0 to 1 and it was determined in which of the new random number intervals this number fell. For such an interval, it is known which comonomer must enter the chain. Thus, there is a transition from the assumption of the equally probable participation of comonomers in the formation of a chain to the assumption of its dependence on the energy necessary for changing the conformation of the dihydrocycle, i.e., the Boltzmann weighting factor.

Table 7 shows the values of Kuhn's segments, calculated for six copolymers with different substituents both for the equally probable participation of comonomers with different torsion angles of the dihydrocycle, and taking into account the Boltzmann factor. As can be seen from the table, for all polymers, with the exception of the first one, values of Kuhn segments, related to the Boltzmann distribution, are slightly less than equiprobable. This is in good agreement with that shown in Fig. 4 by the dependences of the Boltzmann weighting

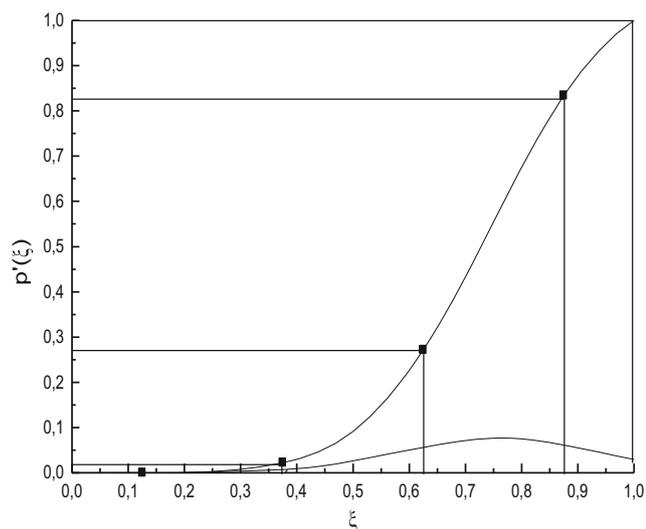


Fig. 3. The curve of inclusion of comonomer probability in the polymer chain

factor on ξ for dihydrocycles with different substituents (Fig. 4). This figure shows that the probability of the existence of comonomers with strongly distorted angles is greater than flattened ones.

Due to the fact that for a polymer containing compound 1, the maximum of the $p''(\xi)$ curve is located approximately in the middle of the considered interval of variation of the torsion angle φ , the Kuhn segment values corresponding to the equally probable and Boltzmann distributions are close. The maximum of the $p''(\xi)$ curve for the polymer containing fragment 2 is strongly shifted to the right, i.e., in the area of strongly distorted cycles for which Kuhn's segments are the smallest. Therefore, for this polymer, the value of the Kuhn segment, taking into account the Boltzmann factor, is substantially less than the equiprobable one. For the other polymers, the $p''(\xi)$ curves are very close to each other, and their maxima are approximately in the middle between the two described above. Obviously, the corresponding Kuhn segments, taking into account the Boltzmann factor, are slightly lower than the equiprobable ones.

Previously, a new class of heat-resistant heterocyclic polymers—polyquinoxalinoquinolines based on bis-benzoxazinones and bis-*o*-aminobenzophenones [38]—was synthesized. To carry out a conformational analysis of polymers based on a heterocycle (Scheme 7), X-ray diffraction study of the crystal structure of the compound 5-14-diphenyl-3,12-dichloro-7.9a, 16.18a-tetrazabenz[*a*, *l*]pentaene-9,18-diol was performed in [39]. It showed that the central heterocycle can have a non-planar equilibrium conformation and has high conformational flexibility. Protonation of such molecules leads to further decomposition of the dihydrocycle and decrease its rigidity. This can have a significant impact on the physicochemical properties of polymers containing condensed heterocycles in the main chain.

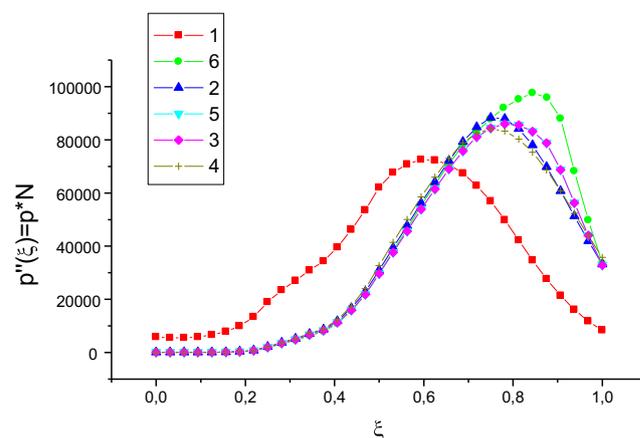
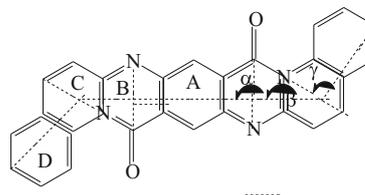


Fig. 4. Dependences of the Boltzmann factor (N is the total number of comonomers involved in the reaction) on the reduced bending angle of the dihydrocycle (ξ) in copolymers. (The numbering of the curves corresponds to that of the compounds in Table 7)



where α - the angle between the A and B planes, β - the angle between the B and C planes, γ - the angle between the C and D planes.

The main quantitative characteristic of such rigid-chain polymers is the value of the Kuhn segment. The Kuhn segments were calculated using the Monte Carlo method under the assumption of free rotation around virtual links and various angles between them (Scheme 7). The high conformational flexibility of the dihydrocycle leads to the fact that units with various degrees of folding can be present in the polymer. However, depending on the signs of the two torsion angles $=C=N-C(=O)-C=$, the elementary unit of the macromolecule may be in the form of a distorted “boat” (*cis* conformation) or a distorted chair (*trans* conformation). In order to assess how the presence of non-planar cycles affects the rigidity of a polymer, a polymer consisting entirely of monomer units in *cis* or *trans* conformation with a specific torsion angle $=C-N-C(=O)-C=$ was considered. Table 8 shows the results of these calculations.

From the data of Table 8, it is clear that polymers are sensitive to changes in the conformation of the dihydrocycle.

In the real polymer, there are dihydropyrimidine rings with different values of torsion angles. In this case, the polymer can be considered as a copolymer consisting of units with a continuous spectrum of torsion angles. To simulate a real macromolecule, consider a polymer that includes all seven types of monomer units (Table 8). If we assume that each type of link is equally likely to be in the polymer chain, then the Kuhn segment of the copolymer will be 1632 Å.

Table 8 Geometric characteristics of repeat units (Scheme 7), Kuhn segment

Conformation	Torsion angle C = N–C(=O)–C	l_0 , Å	α °	β	γ	A_{fr} , Å
<i>trans</i>	$\pm 13.6^*$	18.66	172.9	173.0	172.5	1083
<i>cis</i>	10	18.68	174.3	173.5	178.4	2566
<i>trans</i>	10	18.67	175.0	174.2	172.7	∞
<i>cis</i>	20	18.64	169.4	171.2	172.7	731
<i>trans</i>	20	18.64	169.3	171.2	172.8	∞
<i>cis</i>	30	18.62	163.9	168.4	174.0	533
<i>trans</i>	30	18.61	163.7	168.1	173.9	∞

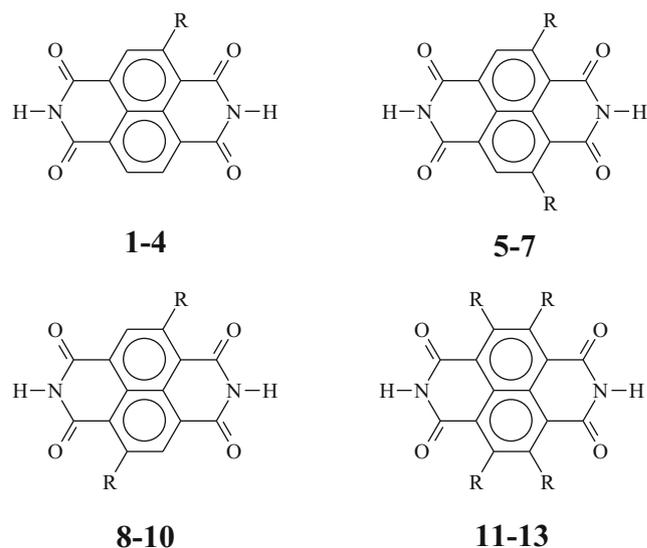
*The value of the torsion angle corresponding to the equilibrium conformation

Overcoming the non-planarity of a heterocycle

Using the example of PNI, it was shown in [38] that in order to obtain an even more rigid polymer based on PNI, it is necessary to select such substituents at a central heterocyclic fragment which, thanks to steric or electronic effects, could create the necessary conditions to increase the equilibrium rigidity of the polymer chain. For this purpose, a series of PNIs with various Schema substituents in the naphthoylenic core was considered (Scheme 8).

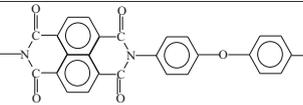
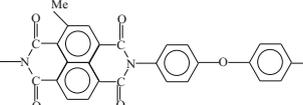
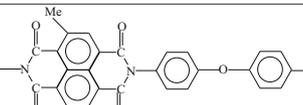
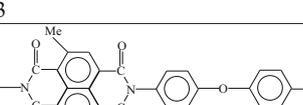
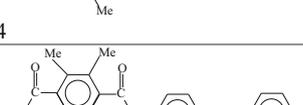
A conformational analysis of these compounds was carried out by scanning the $Cars-C(=O)-NH-C(=O)$, (φ) torsion angle in the interval of $\pm 40^\circ$ with 10° increments and the optimization of the other geometric parameters of the molecules at each step. (Table 9). Two dihedral angles in all molecules changed simultaneously with either one sign (i.e., $+20^\circ$ and $+20^\circ$) or opposite sign (i.e., $+20^\circ$ and -20°).

The equilibrium conformation of imide cycles in almost all substituted molecules is flat. An exception is *cis*- and *trans*-*tret*-Bu of substituted molecules and all tetrasubstituted analogs, when the equilibrium geometry of the imide cycle is in a



Scheme 8 A series of PNIs with various Schema substituents

Table 9 Conformation parameter naphthoylenimide fragment and polymer based on it

Monomer unit	φ_1 , grad	$\Delta\Delta H_f^{293}$, kcal/mol	A_{fr} , Å	Distribution types	
				A_{eq} , Å	A_{bolz} , Å
 1	0	0	74.82	72.63	73.40
	10	0.64	69.71		
	20	2.57	53.64		
	30	5.91	42.03		
	40	10.83	30.39		
 2	0	0	71.45	70.73	66.82
	10	0.63	65.71		
	20	2.54	53.41		
	30	5.84	44.84		
	40	10.72	30.30		
 3	0	0	76.36	72.60	75.11
	10	0.59	65.72		
	20	2.42	53.58		
	30	5.59	44.50		
	40	10.31	30.11		
 4	0	0	73.13	73.10	75.21
	10	0.62	65.71		
	20	2.50	52.11		
	30	5.77	41.46		
	40	10.60	30.64		
 5	0	0.04	75.45	72.00	74.90
	10	0.26	72.15		
	20	1.55	68.10		
	30	4.06	62.77		
	40	7.99	57.00		

twist conformation. The *twist* conformation can be described so that the aromatic atoms of carbon and nitrogen lie in the plane of the ring, and the carbonyl groups deviate in opposite directions. Such a distortion of the imide ring in the studied molecule is obviously due to the unfavorable thermal interaction between bulky groups and neighboring C=O fragments.

It is worth noting that the conformations of an “elongated boat” and an “elongated chair,” which are formed during the bending of imide rings, are almost equivalent in energy, that is, almost the same energy is required to bend a molecule with torsion angles of $++20^\circ$ or $+--20^\circ$. That is why in Table 9 are given only those energy changes in molecules that correspond to scanning C(Ar)–C(=O)–NH–C(=O) torsion angles with equal values.

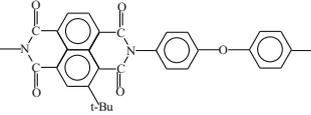
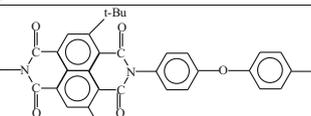
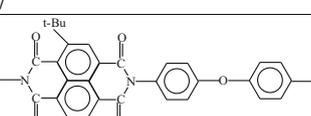
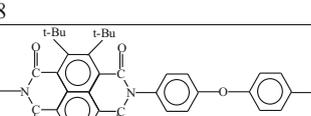
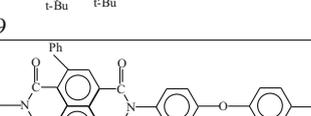
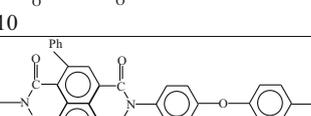
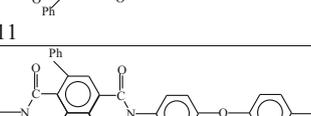
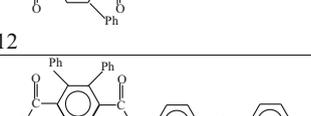
As can be clearly seen from Table 9, the introduction of a volume substituent in the second position of the naphthalene cycle, this practically does not lead to an increase in the conformational flexibility of diimide rings. Only in the case of the phenyl-substituted analog, a slight increase in its flexibility is observed in comparison with the initial unsubstituted molecule. On the contrary, when describing the conformational characteristics of disubstituted molecules (*cis* and *trans*), there is a noticeable increase in the conformational flexibility of

imide cycles when the volume of the steric substituent increases.

The *trans*-di-Me-substituted molecule has the same flexibility as the *cis*-di-Me molecule, whereas for di-Ph and di-*tert*-Bu molecules one can observe a slight increase in the conformational flexibility of the molecules with an increase in steric volume. The most flexible molecule among all studied substituted naphthoylenedimides is the tetra-Ph compound. But this is an energy characteristic, showing the ability of the cycle to be distorted, and the flexibility of the imide ring itself does not demonstrate itself the geometry of the first one.. As mentioned above, the imide cycles in substituted molecules assume the elongated conformations of a “chair” or “boat,” where the dihedral angle C(Ar)–C(=O)–NH–C(=O) is not zero. However, in the case of tetrasubstituted compounds, a completely different situation is observed. Below, the Newman projection along the N–N line demonstrates the geometry of the molecules.

Scheme 9 shows a projection of a tetra-Ph-substituted molecule, where the N atoms lie in the plane of the naphthalene cycle, and the carbonyl groups deviate from this plane, forming such a cross in the diagram. On the contrary, in the case of tetra-Me and tetra-*tert*-Bu derivatives, the nitrogen atoms deviate from the plane of the

Table 9 (continued)

6		0	0	70.19	71.26	72.11
		10	0.54	62.26		
		20	2.36	49.47		
		30	5.58	38.47		
		40	10.72	27.48		
7		0	0.62	70.08	71.46	73.36
		10	0.42	68.96		
		20	1.48	64.42		
		30	3.90	53.09		
		40	7.88	41.70		
		14.3eq	0	71.36		
8		0	0.55	74.37	68.33	65.24
		10	0.41	57.29		
		20	2.08	45.13		
		30	5.15	35.20		
		40	9.85	23.81		
		2.0eq	0	63.39		
9		0	0.13	71.78	71.32	68.73
		10	0.07	71.83		
		20	0.97	67.15		
		30	3.09	63.11		
		40	6.66	53.80		
		6.0eq	0	73.09		
10		0	0	73.02	72.70	74.22
		10	0.55	70.17		
		20	2.24	66.08		
		30	5.16	61.55		
		40	9.57	55.10		
11		0	0	75.07	70.41	73.60
		10	0.50	68.63		
		20	2.10	62.11		
		30	4.91	53.08		
		40	9.19	44.63		
12		0	0	77.65	72.47	73.28
		10	0.59	65.64		
		20	2.41	53.04		
		30	5.56	41.22		
		40	10.23	30.18		
13		0	0.01	77.70	74.13	77.06
		10	0.19	74.63		
		20	1.22	71.16		
		30	3.39	66.04		
		40	6.94	57.52		

Scheme 9 A projection of a tetra-Ph-substituted molecule

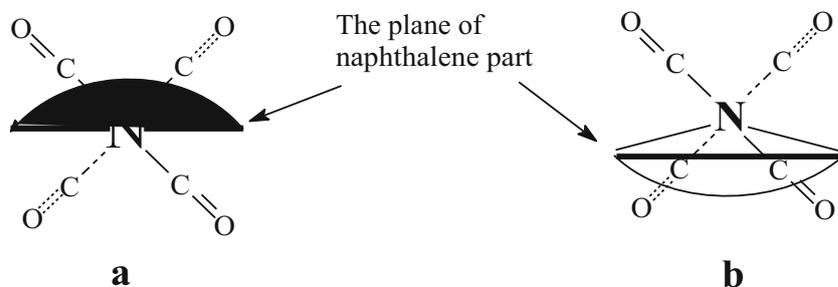
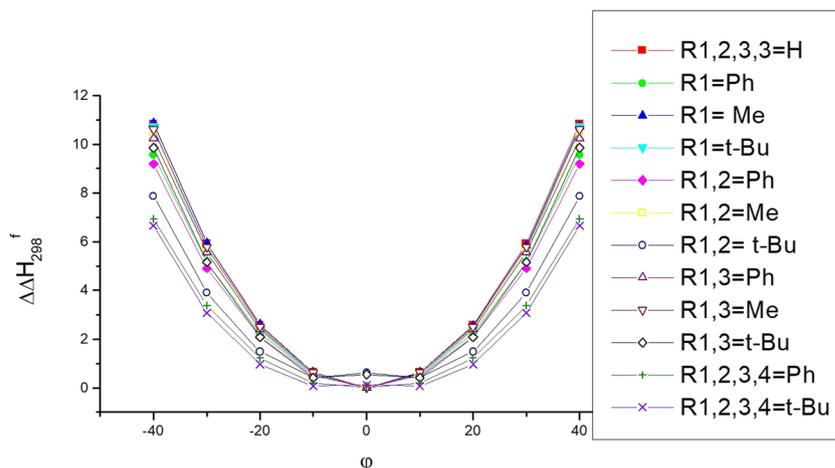
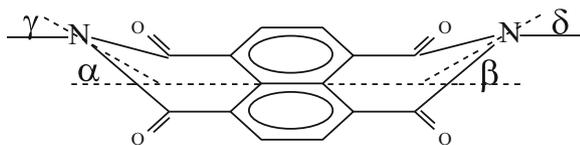


Fig. 5 The change in the energy of a molecule during bending of a naphthoylenimide fragment with different substituents at the changing of the torsion angle φ



naphthalene cycle, but the C=O groups also form a cross. These diagrams show that the distortion of the tetra-Ph-substituted naphthalene cycle is less significant.

As can be seen from Table 9, a change in the angle φ by more than 40° requires already considerable energies, exceeding the possible energy input during the course of the reaction at elevated temperatures. In addition, Fig. 5 shows that, on the basis of the dependences $\Delta\Delta H_f^{298}(\varphi)$, it is difficult to conclude that one of the substituents has a preferential effect on the rigidity of the naphthoylenimide fragment



As we said earlier, the decrease in the stiffness of the PNI is determined by the presence of rings in the polymer chain in the elongated conformation of the “boat.” The geometry in this ring conformation is described by the four angles α , β , γ , and δ . The greater the depth of the “boat,” the greater the total angle the polymer chain is turned. Thus, the conformational rigidity of the polymer as a whole was determined only by chemical changes in the naphthalene fragment. In this series of polymers, more flexible polymers correspond to a shorter Kuhn segment length, and the source of flexibility of the polymer is the central heterocyclic fragment (Table 9).

To determine which polymer should be the most rigid with the same energy expended, the dependence $\Delta\Delta H_f^{293}(A_{fr})$ was calculated for different values of φ . As can be seen from Fig. 6, the most rigid PNI is a polymer with four phenyl groups on the naphthalene moiety of the naphthoylenimide fragment.

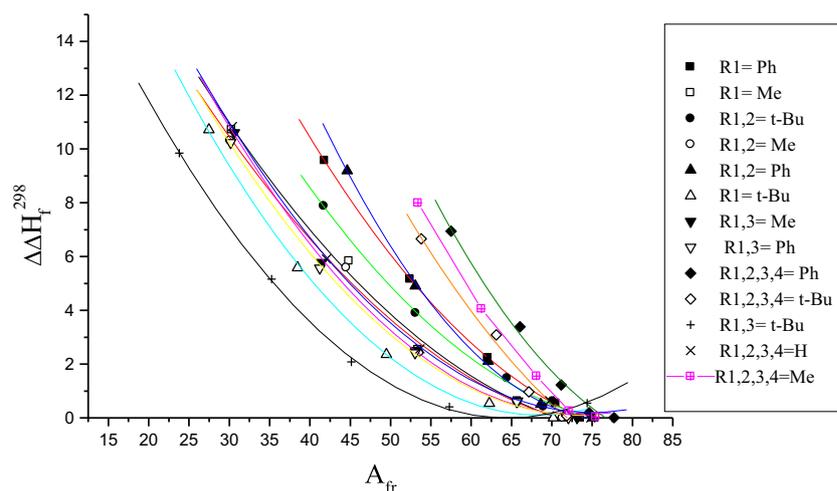
For example, using 2,3,6,7-tetraphenyl substituted 1,4,5,8-naphthalenetetracarboxylic acid dianhydride in the synthesis of the polymer PNIQ tetraphenyl, it is possible to obtain a much more rigid polymer than without these substituents. For such a polymer containing 15% of units with a diimide moiety in the conformation, the “boat” with an angle of $\varphi = 20^\circ$, Kuhn’s segment is 3200 Å, and for PNIQ without substitutes with the same content of units in the conformation, the “boat” with the same angle of φ is only 1200 Å.

Therefore, in order to evaluate which of the substituents at the expended energy leads to the least distortion of the ring in the case of PNI, we used again the concept of the Kuhn segment as a measure of the rigidity of the polymer chain. For this, the Kuhn segment values were calculated under the assumption of free rotation, A_{fr} [8]. The PNI structural unit contained the same constant fragment—diphenylether and one variable fragment of the naphthoylenimide cycle, containing various substituents in the naphthalene core. Thus, the equilibrium rigidity of the polymer as a whole was determined only by chemical changes in the naphthalene cycle. In this series of polymers, more flexible polymers correspond to smaller Kuhn segment values, the source of flexibility of which is central heterocyclic fragments (Table 9).

In order to estimate which of the polymers at the expenditure of the same energy will be the most rigid, the dependence of $\Delta\Delta H_f^{298}$ on A_{fr} was built at different values of the angle φ . From Fig. 6, it can be seen that the most rigid PNI will be a polymer with four phenyl rings as substituents.

However, in a real polymer, the naphthoylenimide fragment included in the polymer chain has different C(Ar)–C(=O)–N–C(=O) torsion angles in the cycle. Therefore, to calculate the Kuhn segment of realistic polymer containing naphthoylenimide fragment with

Fig. 6 The dependence of the energy change at the bending of naphthoyleneimide cycle with different substituents from the polymer rigidity



one of the abovementioned substituents, we shall describe it as a polymer consisting of a sequence of comonomers. In these comonomers, the naphthoyleneimide fragment takes the different values of the dihedral angles in the interval under study. We studied nine isomers, because a cycle can equiprobably take both an “extended boat” and an “extended chair.”

For these calculations, the technique described above was used (Eqs. 3, 4, and 5). To calculate the content of each comonomer in the polymer, we interpolated the $\Delta\Delta H_f^{298}(\varphi)$ dependence every 1.25° and used it to calculate the function $p(\varphi)$ (Fig. 7).

As it can be seen from Fig. 7, the behavior of the Boltzmann weighting curve contradicts the behavior of the potential energy curve. For example, at low energies, the probability of the presence of the corresponding comonomers is significantly higher compared to comonomers with a higher potential energy. The calculation of the Kuhn segment usually requires the generation of 500 chains consisting of 2500 structural units, i.e., it is necessary to use 1,250,000 units of different comonomers. The $p(\varphi)$ curve was multiplied by this value and divided into nine parts. In a polymer, the number of comonomers

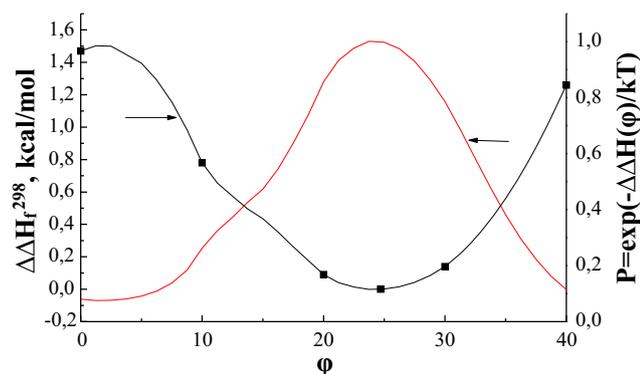


Fig. 7 The dependences $\Delta\Delta H_f^{298}(\varphi)$ and $p(\varphi)$

with a given value of the torsion angle $C(\text{Ar})-C(=O)-\text{NC}(=O)$ is equal to the sum of the ordinates $p(\varphi)$ within the selected interval (Fig. 7). Angles were expressed in radians and normalized to maximum values. Then the probability of the presence of each comonomer in the polymer chain was determined as follows. A uniformly distributed random number was generated in the range from 0 to 1, and the angular interval containing this number was determined. For each interval, it is known how many comonomers with a given dihedral angle should be included in the polymer chain (Fig. 8). If all such comonomers were exhausted, then a new random number was generated corresponding to those intervals for which the comonomer is not yet exhausted. Thus, we have moved from the equally probable appearance of comonomers to their appearance with the Boltzmann factor

For PNI, the equilibrium state is a flat or almost flat imide fragment (Fig. 9). As can be seen from Table 9, in this case the Boltzmann value for the Kuhn segment is slightly higher than the equiprobable one, with the exception of the case when the equilibrium state of

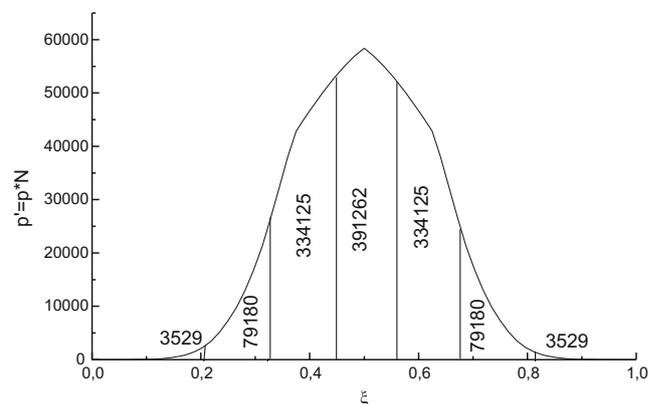
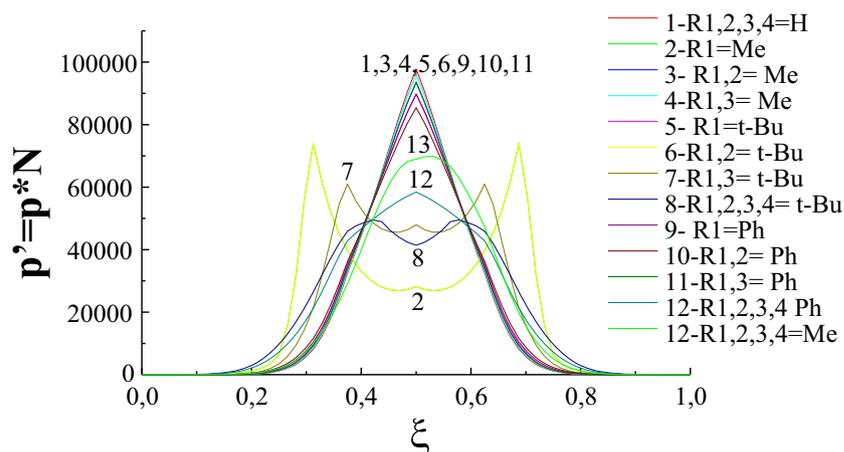


Fig. 8 The number of units, with given φ dihedral angle (with consideration of the Boltzmann weight factor), included into polymer chain $p'(\xi)$

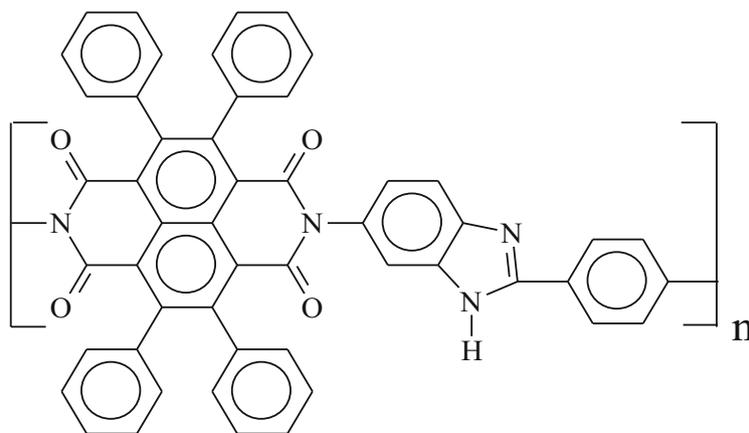
Fig. 9 The dependences (with consideration of the Boltzmann weight factor) $p'(\xi)$ at different substituents in the central heterocyclic fragment.



PN1 is slightly offset from the flat imide fragment. It should be noted that chair-type conformational isomers make a significant contribution to polymer rigidity.

The rigidity of the PN1Q, taking into account the Boltzmann factor without substituents in the naphthalene ring, is 1770 Å, and with four phenyl substituents, it is 4600 Å, i.e., more than three times higher. In the case

of PN1B, which is a less rigid polymer ($A_{fr} = 300$ Å), the Kuhn segment with four phenyl substituents in the naphthalene cycle increases to 1880 Å (taking into account the Boltzmann factor).



If we replace four phenyl groups, then perhaps this will allow chemists to obtain much more rigid polymer materials that are even more durable, such as the unique IPLON family and its copolymers [1, 40–43].

Thus, the use of the proposed calculation technique allowed in the present work to create a new approach to the calculation and analysis of factors affecting the conformation of the chain of rigid-chain polymers. Using the developed method, it is possible to predict the potential of various condensed heterocyclic systems from the point of view of obtaining rigid chain polymers on their basis and to carry out their molecular design in order to obtain the most rigid structures. Products made from such polymers (films, fibers)

can have record-breaking strength characteristics in comparison with the known ones.

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