Physical Chemistry

The effect of side substituents on rotation hindrance in polyheteroarylenes

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Hindered rotation was considered in calculations of the conformational parameters of a series of polyheteroarylenes with bulky side substituents by the Monte-Carlo method. Within the range of experimental errors, the results of calculations for several polyarylates coincide with the values of conformational rigidity, determined from hydrodynamic experimental data. The proposed procedure was used to estimate the rigidities of a number of polymers with bulky side substituents for which experimental determination is difficult.

Key words: conformational analysis, Kuhn segment, hindered rotation, polyheteroarylenes, side groups.

Previously we studied the conformation parameters of aromatic heterochain and heterocyclic polymers assuming that rotation is free.[1—4] It was found that with the exception of polymers with bulky side groups, the experimental values for the Kuhn segment (A_{exp}) for polyheteroarylenes virtually coincide with those calculated with the assumption of free rotation (A_{fr}). The introduction of bulky side groups into the polymer backbone should increase its rigidity, because the rotation becomes hindered. In this case, the assumption of free rotation is no longer valid, and it is necessary to take account of hindrance, *i.e.*, to calculate A_{rot}.

The main conformation parameter is the statistical Kuhn segment:

$$A = \lim_{n \to \infty} \left(\frac{< R^2 >}{nl_0} \right),$$

here $<R^2>$ is the root-mean-square distance between the ends of a polymer chain, averaged over all the possible conformations; $L = nl_0$ is the contour chain length, *i.e.*, a parameter independent of the chain conformation; l_0 is the contour length of a repeat structural unit. For polyheteroarylenes where a macromolecule unit contains virtual bonds of various lengths arranged at various angles, the contour length is taken to be the length of a broken line connecting the centers of these bonds. In this case, l_0 does not depend on the chain conformation and can serve as a measure of the length of the macromolecule.

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Yet another frequently encountered characteristic is the hindrance parameter

$$\sigma = \sqrt{A_{exp}/A_{fr}}.$$

When the Kuhn segment is calculated assuming free rotation, the side substituents are not taken into account. The validity of this assumption for this class of polymers has been proven previously.[6,7]

In the present work, we consider the effect of side substituents on the conformational rigidity and propose a method for the calculation of conformation parameters with allowance for the effect of side groups. In the calculations based on the assumption of free rotation, we used the Monte-Carlo method[2] according to which the random numbers for chain generation are evenly distributed in the $[0.2\pi]$ range. Taking into account the hindrance of rotation, random numbers cannot be considered as evenly distributed, because in the presence of a side substituent, only those conformations are realized in which the distances between non-bonded atoms in a structural unit do not exceed the sum of their van der Waals radii. In this case, the probability of rotation through angle φ around a virtual bond depends on the form of the potential energy function $U(\varphi)$. To take this into account in the construction of chains, we introduced a function of distribution over the internal rotation angles $F(\varphi)$ with weights proportional to the Boltzmann factor $\exp(-U(\varphi)/kT)$,[8] and random number were generated in conformity with this function. If the structural units are closely spaced, some angles of rotation are never encountered, and some others occur in rare cases and, with is most probable, in the absence of steric interactions between structural units.

To test the proposed method, we have chosen a number of polyarylates with various sizes and positions of side substituents, for which experimental values for the Kuhn segment are known. Dilute solutions of these polymers have been studied previously by light scattering,[3] and the results can be used to compare the calculated A_{rel} values with those found experimentally. Table 1 contains the structural units and the Kuhn segment values for the polyarylates studied, found experimentally, and calculated with allowance for hindrance. The hindrance parameters σ are also included. To consider the difference between the size of the side groups, we introduced the value M_L/M_{L_0}, where M_{L_0} and M_L are the ratios of the molecular weight of a polyarylate unit to its contour length in the absence of the substituent and with allowance for the molecular weight of the substituent, respectively. It can be seen from Table 1 that increasing the volume, and, hence, the weight of the substituent tends to enhance hindrance to the rotation. However, this approach does not take into account the position of the substituent in the polymer chain.

The polyarylates presented in Table 1 can be divided into two groups depending on whether substituents are located in the phenyl ring of the backbone (1) or at the bridging C atom (2).

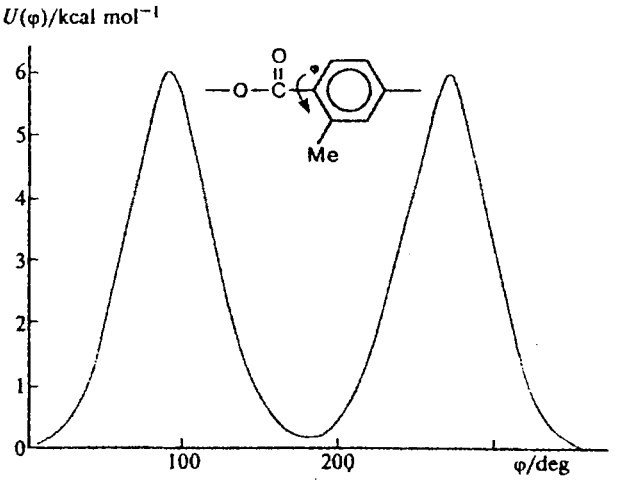


Fig. 1. Dependence of the potential energy $U(\varphi)$ on the angle of rotation around the Ph_1—C virtual bond in polymers with a side group in the backbone.

Figure 1 shows the angular dependence of $U(\varphi)$ for a polyarylate fragment containing a side substituent in the phenyl ring of the backbone. The $U(\varphi)$ function was calculated by the MM3 method;[5] the φ angle was varied from 0 to 360° with as step of 5°, the other geometric parameters of the macromolecule fragment were optimized. Since the substituent at the bridging C atom is asymmetrical, the potential energy function $U(\varphi_1, \varphi_2)$ for compounds of the second group depends on the angles of rotation around the Ph_1—C and Ph_2—C bonds, φ_1 and φ_2.

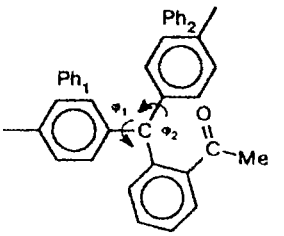


Figure 2 shows this dependence for the polyarylate fragment presented in Table 1 (line 5). The initial conformation with angles φ_1 and φ_2 equal to zero, corresponds to the *trans*-chain. In the initial conformation, the benzene ring of the side group attached to the bridging C atom lies in the plane perpendicular to the image plane.

For all the polymers listed in Table 1, we calculated the conformation energy as a function of the angle of rotation, $U(\varphi)$, and the A_{rel} values. The A_{exp} values for these polymers were found by light scattering and viscosimetry from the hydrodynamic properties of dilute solutions of these polymers in poor solvents.[3] Comparison of the A_{rel} and A_{exp} values implies that the data obtained by our method are in good agreement with the experimental results for a number of polyarylates and can be used to estimate the rigidity of polymers, for which determination of the A_{exp} values is very difficult.

Table 1. Conformational parameters of polyarylates

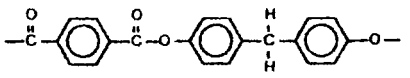
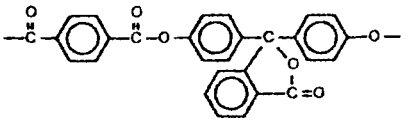
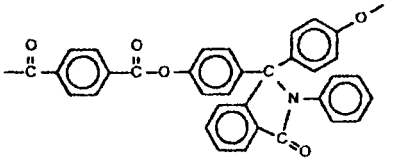
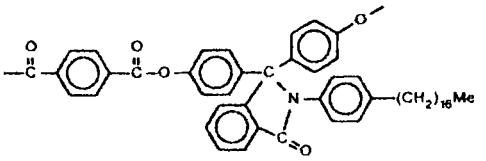
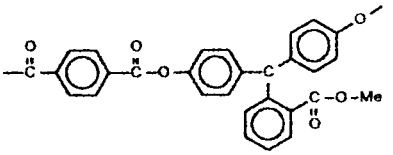
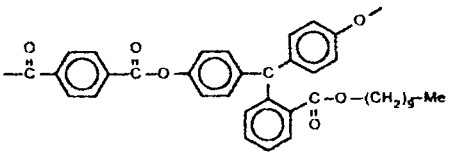
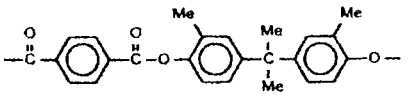
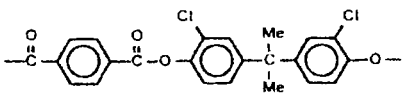
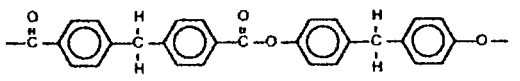
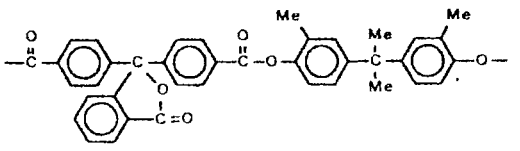
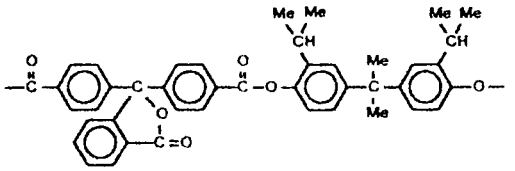
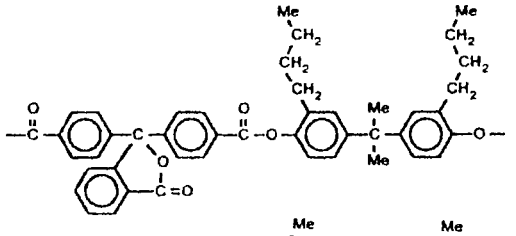
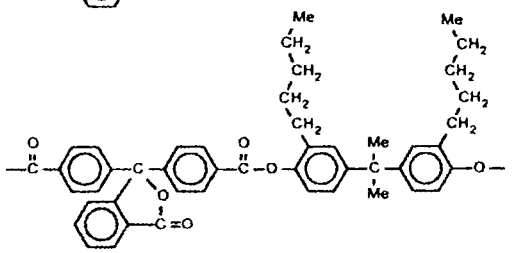
Structural unit	M_L/M_{L_0}	A_{rel}/Å	A_{exp}/Å	σ
	1.0			1.0
l_0 = 17.5 Å, A_{fr} = 25.7 Å				
	1.36	36.1	36.4 (THF) 40.8 (CP)	1.19—1.26
	1.59	42.1	42.1 (CP)	1.28
	2.16	58.8	58.0 (θ) 61.4 (CP)	1.50—1.54
	1.40	37.1	37.3 (THF) 37.8 (DO)	1.20—1.21
	1.79	47.6	47.3 (CP) 51.4 (THF)	1.36—1.41
	1.08	26.6	27.8 (TCE)	1.00
	1.19	37.0	38.2 (TCE)	1.20
	1.00			1.00
l_0 = 22.5 Å, A_{fr} = 19.2 Å				
	1.12	23.5	24.9 (TCE)	1.15

Table 1. (continued)*

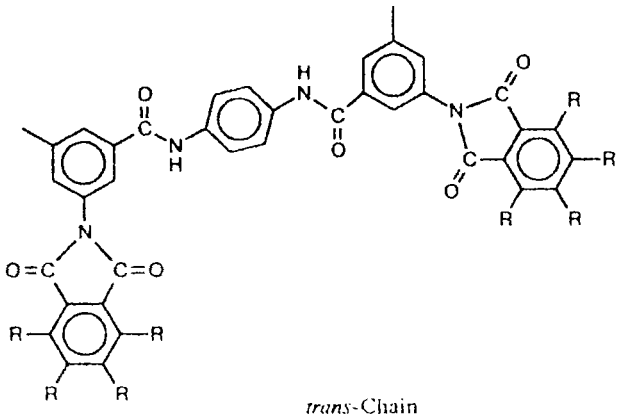
Structural unit	M_L/M_{L_0}	A_{rel}/Å	A_{exp}/Å	σ
	1.35	38.2	39.0 (TCE) 41.4 (TCE)	1.42—1.47
	1.35	34.0	33.8 (TCE) 34.2 (TCE)	1.32
	1.40	41.8	43.9 (THF) 48.5 (TCE)	1.51—1.59

Note. The solvents are given in parentheses: DO is dioxane; CP is chloroform; THF is tetrahydrofuran; TCE is tetrachloroethylene, and θ is a solvent corresponding to the θ conditions.

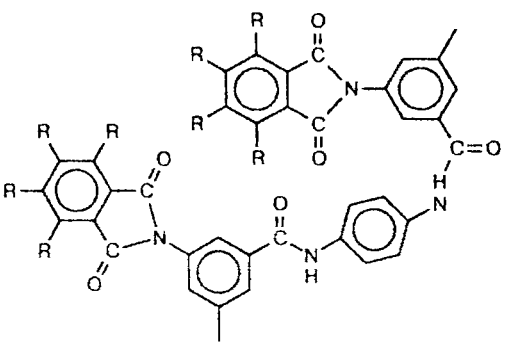
For some polymers, the experimental determination of the rigidity is impossible because of the poor solubility. However, the same polymers possess unique thermal and electric properties, which should correlate with their conformational rigidity. Therefore, it is of interest to calculate the rigidity for these polymers by the above-proposed method.

Tables 2—5 include polymers containing substituents in the backbone phenylene rings and the relevant Kuhn segments A_{fr} calculated neglecting the side groups. More detailed analysis of the geometric structures of the side substituents reveals that these polymers contain substituents of three types. The first type is a phthalimide ring in the *meta*-position to the carbonyl fragment of the backbone (see Table 2), the second type is represented by the phenyl groups in the *ortho*-position in relation to the quinoxaline ring (see Tables 3 and 4), and the third type is a phenoxide side group (see Table 5).

The structures of the first-type side group (phthalimide ring in a polyamide chain) in *trans*- and



trans-Chain

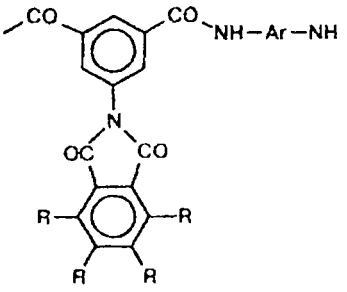


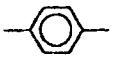
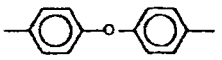
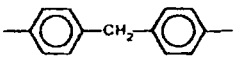
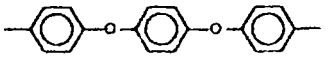
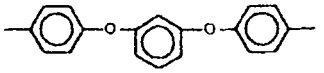
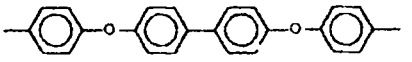
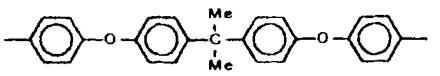
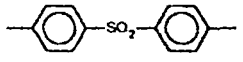
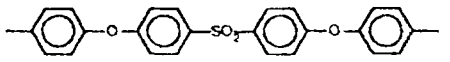
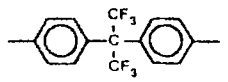
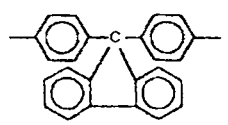
cis-Chain

cis-chains are substantially dissimilar. In both cases, the distance between two side groups (phthalimide rings) is much greater than the sum of the van der Waals radii, and the rotation does not become hindered. The rotation around the CO—Ph bond could be hindered due to the fact that the distance between the closest carbonyl groups in the benzimide ring of the side substituent and in the amide fragment of the backbone is ~2.5 Å in both chains; this is somewhat shorter than the sum of the van der Waals radii of two O atoms. However, this does not lead to substantial hindrance to rotation, because the phthalimide fragment is preferably arranged perpendicular to the plane of the benzene ring attached to it. Consequently, the distance between the amide and imide carbonyl groups increases to 3.5 Å, which is greater than the sum of the van der Waals radii of two O atoms. Thus, the introduction of a phthalimide ring as the side substituent into the polymer chain should have no effect on the Kuhn segment length of the polymers (see Table 2), and A_{fr} can serve to characterize the conformation of these polymers.

The side groups of the second type are phenyl rings in the quinoxaline fragment linked to the quinoxaline cycles. In this case, the hindrance to rotation largely

Table 2. Conformational parameters of polyamides with phthalimide side substituents



Structural unit	l_0/Å	A_{fr}/Å
Ar = 	12.6	36.4
	17.6	31.4
	17.4	25.2
	22.3	28.7
	22.8	20.6
	26.4	30.5
	27.2	22.7
	17.8	21.6
	27.5	24.1
	17.4	25.1
	17.5	25.4

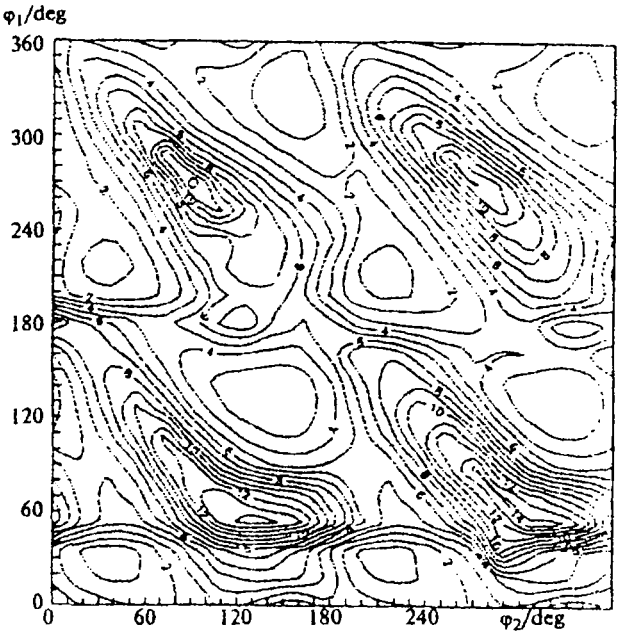
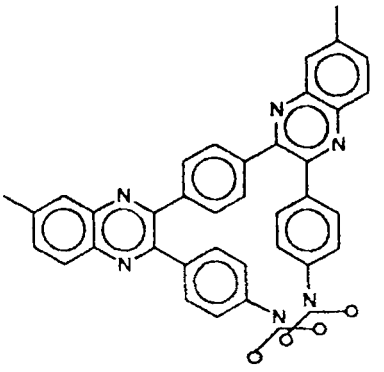


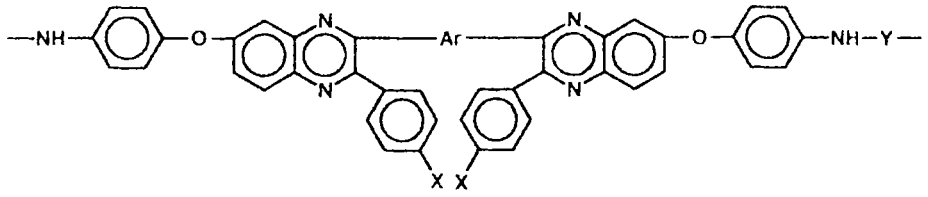
Fig. 2. Dependence of the potential energy ($U(\varphi_1, \varphi_2)$ /kcal mol^{-1}, denoted by numerals) on the angles of rotation in a fragment with a side substituent at the bridging atom of the polyarylate backbone.

The side groups of the second type are phenyl rings in the quinoxaline fragment linked to the quinoxaline cycles. In this case, the hindrance to rotation largely

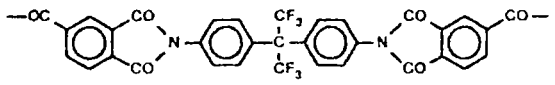
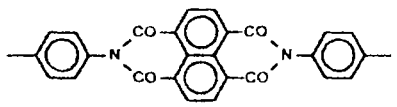
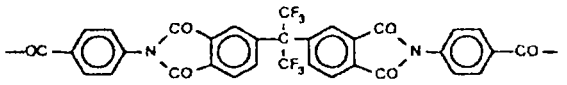
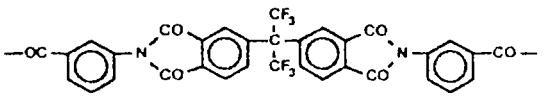
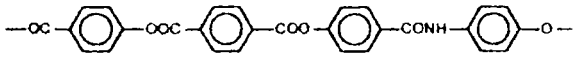
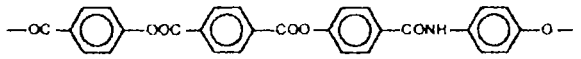


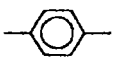
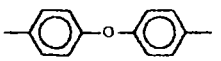
cis-Conformation

Table 3. Conformational parameters of polymers



X = H, NO_2

Structural unit	l_0/Å	A_{fr}/Å	A_{rot}/Å for X		σ
			X = H	X = NO_2	
Y_1 = 					
Ar_1	52.4	35.6	39.2	42.1	1.10 1.18
Ar_2	57.3	33.9	34.6	37.2	1.02 1.10
Ar_3 = 	64.9	42.6	42.6	42.6	1.00
Y_2 = 					
Ar_1	53.1	35.5	38.7	41.5	1.09 1.17
Ar_2	58.0	34.0	34.7	37.4	1.02 1.10
Y_3 = 					
Ar_1	52.4	25.7	28.3	30.3	1.09 1.17
Y_4 = 					
Ar_1	47.9	44.3	48.8	52.3	1.10 1.18
Ar_2	52.8	43.4	44.3	47.7	1.02 1.10
Y_5 = 					
Ar_1	47.7	34.6	38.1	40.5	1.10 1.17
Ar_2	52.6	33.5	34.2	36.8	1.02 1.10

Note: Ar_1 =  ; Ar_2 =  .

depends on the length of the bridge between the quinoxaline cycles. Benzene ring is the shortest bridge among those considered in our study (see Table 3). In this case, the side groups closely approach one another.

When the phenyl bridge between the quinoxaline fragments is replaced by a diphenyl oxide or a diphenylnaphthoyleneimide bridge, the distance between the quinoxaline rings increases, and the side groups are arranged freely without interfering with one another; even the presence of NO_2 groups in the diphenylnaphthoyleneimide fragment does not enhance the rotation hindrance. For the fragment with phenyl bridges, we calculated the dependence of the conformation energy $U(\varphi)$ on the angle of rotation φ around a virtual

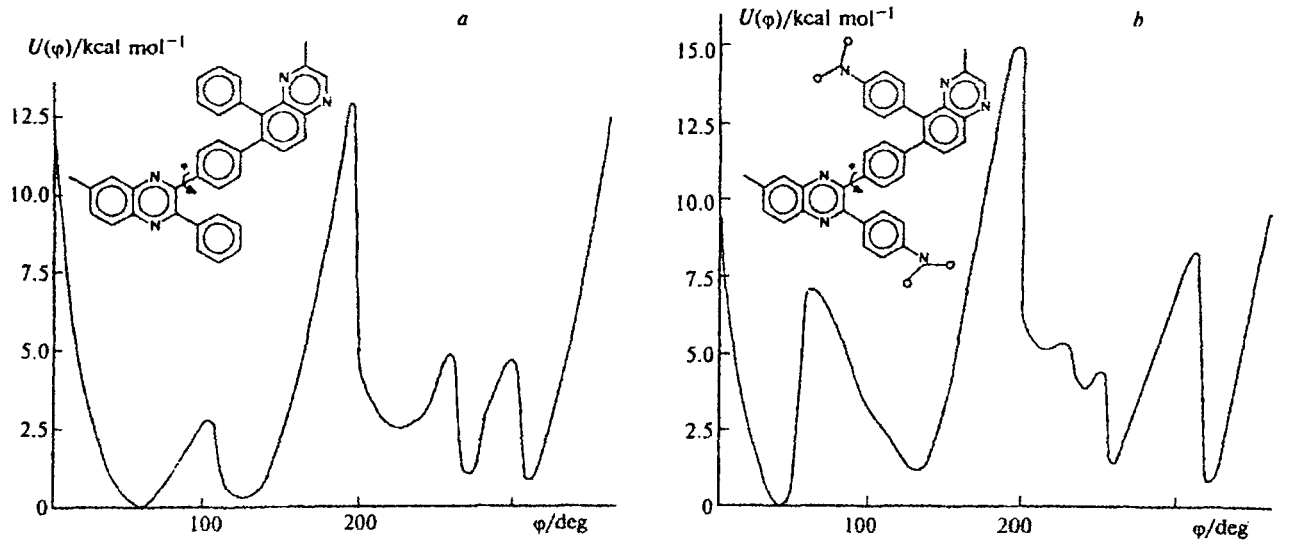
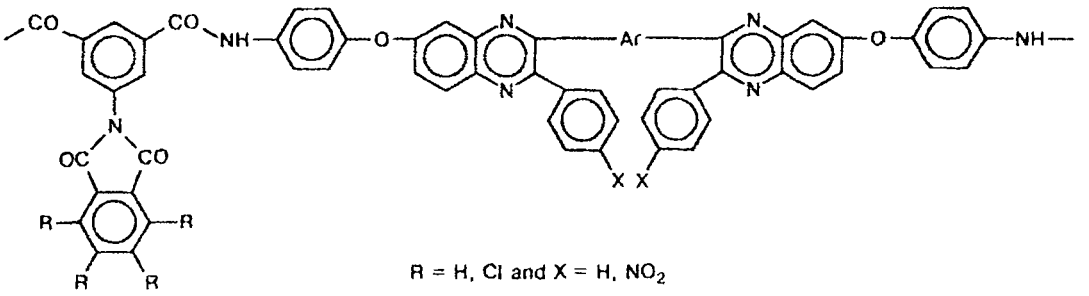
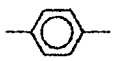
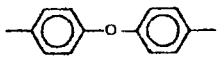
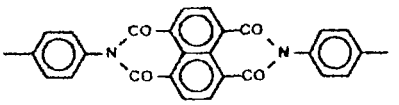


Fig. 3. Dependence of the potential energy $U(\varphi)$ on the angle of rotation around the virtual bond between two quinoxaline rings with phenyl (*a*) and 4-nitrophenyl (*b*) as the side groups.

Table 4. Conformational parameters of polymers



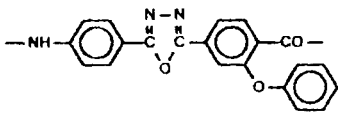
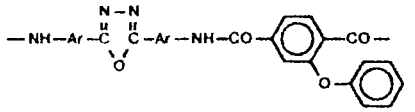
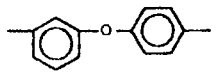
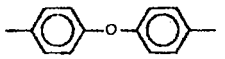
R = H, Cl and X = H, NO_2

Structural unit	l_0/Å	A_{fr}/Å	A_{ret}/Å				σ
			R = H, X = H	R = Cl, X = H	R = H, X = NO_2	R = Cl, X = NO_2	
Ar_1 = 	35.0	27.4	30.1	30.5	32.3	32.8	1.10 1.18
Ar_2 = 	40.0	25.8	26.3	27.3	28.3	29.0	1.02 1.12
Ar_3 = 	47.5	37.3	37.3	38.6	39.3	39.7	1.00 1.06

bond between the phenylquinoxaline fragments (Fig. 3, *a*). In this case, the *cis*-chain with $\varphi = 0$ was taken as the initial structure, whereas $\varphi = 180°$ was assigned to the *trans*-conformation.

With 4-nitrophenyl as the side group, rotation becomes more hindered (see Fig. 3, *b*). In both cases (see Fig. 3, *a*, *b*), the $U(\varphi)$ curves clearly demonstrate the presence of two strong peaks (at $\varphi \approx 0$ and $\varphi \approx 180°$) and

Table 5. Conformational parameters of poly-1,3,4-oxadiazolamides containing phenoxyterephthalates

Structural unit	l_0/Å	A_{fr}/Å	A_{rel}/Å, R = H	σ
	9.9	73.4	100.6	1.37
				
Ar = 	20.5	143.5	185.1	1.29
Ar = 	30.2	27.0	33.5	1.24
Ar = 	30.3	51.3	63.6	1.24

a number of weak peaks. For both nonsubstituted and substituted phenyl side groups, the first peak is rather intense (~9—11 kcal mol^{-1}). Thus, for both polymers, the occurrence of conformers in this region is relatively unlikely. The second peak at $\varphi \approx 180°$ (*cis*-conformation) is intense (12—15 kcal mol^{-1}) and asymmetrical in both cases. This confirms the assumption that when a chain with the *cis*-conformation contains side groups, the distance between their H atoms (especially, in the case of 4-nitrophenyl group) is much shorter than the sum of the relevant van der Waals radii. Therefore, after the angle $\varphi = 180° \pm 20°$ with respect to the *cis*-conformation has been attained, the groups cannot continue approaching each other, and there are no conformers in this region either. Thus, the set of conformers for these polymers is depleted, and the molecule becomes more stretched and more rigid.

The values of the Kuhn segment A_{rel}, calculated with allowance for the hindrance to rotation, are listed in Table 3. In all cases, the magnitude of the parameter σ confirmed our hypothesis that in the presence of a short bridge (benzene ring), the rotation hindrance is enhanced, and when 4-nitrophenyl is present as the side group, rotation is even more hindered. However, since in the case of the polymers listed in Table 3, a unit contains a large number of virtual bonds around which free rotation is possible, and only one bond around which rotation is hindered, this has only a slight effect on the final rigidity of the polymer.

Table 4 includes polymers containing side groups of the first and second types. The hindrance parameters for these polyheteroarylenes are close to those for polymers containing only side groups of the second type. Table 5 also presents the conformation parameters for polymers with phenoxide substituents.

In this case, the rotation hindrance is mostly due to the short distances between the H atoms in the phenylene ring of the backbone amide fragment and in the phenylene ring of the side group; thus, the latter tends to be arranged in a plane perpendicular to the image plane. In addition, the rotation hindrance is determined by the proximity of the O atoms in the carbonyl group of the amide fragment and in the ether group of the side substituent. It can be easily seen from Fig. 4 that for the rotation around the Ph—CO bond (angle φ_1), the difference between the energies of the *cis*- and *trans*-confor-

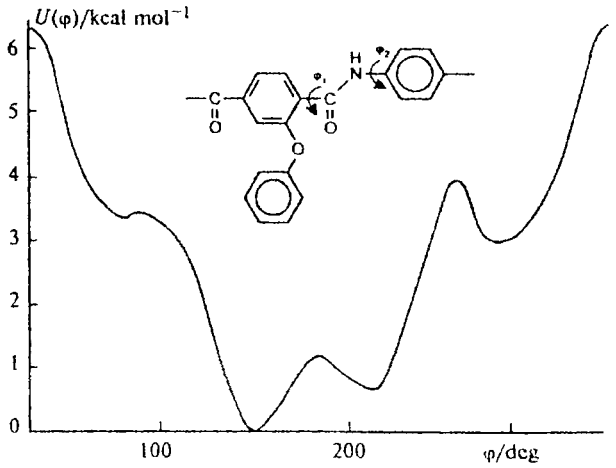


Fig. 4. Dependence of the potential energy $U(\varphi)$ on the angle of rotation for a fragment with a side phenoxide substituent.

mations is close to 6 kcal mol^{-1}, and again the full set of conformers corresponding to free rotation in the polymer chain is not realized. For rotation around the NH—Ph bond (angle φ_2), the angular dependence of the potential energy follows a pattern normal for polyamides.[13] It was found experimentally that a substituent in the *ortho*-position to the carbonyl group accounts for a rotation hindrance described by $\sigma = 1.2—1.5$.[3] The values that we obtained lie in the same range.

It can be seen from the data presented in Tables 1—5 that the introduction of side substituents in a chain does not necessarily result in a substantial rotation hindrance. This occurs only in those cases where the side group cannot be freely arranged in the niche formed by long virtual bonds in polyheteroarylenes, and short (shorter than the sum of the van der Waals radii) contacts between the backbone and side-group atoms arise. Tables 2—5 compare the calculated conformational rigidities of the polymers with their physical characteristics.[14] Estimates of the influence of side groups on the conformational rigidity can be used in the target-directed synthesis of polyheteroarylenes with desirable physical properties.

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