The influence of substituents in the quinone dihydrocycle of anthroneylidene molecules on the polymer chain rigidity

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The effect of substituents on the conformational rigidity of the six-membered dihydrocycle constituting the repeating unit of heterocyclic polymers was studied by the semiempirical AM1 method and by conformational analysis. The polymer rigidity can be controlled over a wide range by choosing appropriate substituents in the dihydrocycle. An original procedure was proposed for calculating the Kuhn segment of the copolymer taking into account the Boltzmann factor.

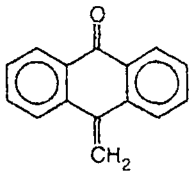
Key words: conformational analysis, quantum-chemical calculations, AM1 method, Monte Carlo method, polyheteroarylenes, Kuhn segment.

Rigid-chain heterocyclic polymers are one of the most interesting classes of organic high-molecular weight compounds. They serve as the basis for producing high-strength, high-modulus films and fibers.[1] The basic requirement for the structure of such macromolecules is their conformational rigidity, which is characterized by the Kuhn segment value. It has been shown[2–4] that high conformational flexibility of the six-membered dihydrocycles constituting the repeating unit can appreciably decrease the Kuhn segment value. Substantial out-of-plane deformations of the monomer unit can be observed even in polycondensed aromatic systems.[5]

Previously,[2–5] only those systems were considered in which the repeating unit has a planar equilibrium conformation. At the same time, it is of interest to assess the influence of the conformational behavior of six-membered cycles on the Kuhn segment value of the macromolecule in the case of nonplanar structure of partially hydrogenated rings. From this point of view, the anthraquinone derivatives, which exhibit interesting photochemical and luminescent properties,[6,7] deserve particular attention. Variations of the conformation of the repeating unit in such macromolecules can appreciably affect their electronic characteristics.[8]

Despite the fact that the six-membered cycle in the *p*-quinone molecule has a planar equilibrium conformation, it is highly flexible.[9,10] Replacement of one carbonyl group by the methylene group causes the partially hydrogenated ring to adopt a boat conformation.[11] Thus, the equilibrium conformation of the six-membered cycle in anthroneylidenes is nonplanar; at the same time, the dihydrocycle should be highly flexible. Thus it is convenient to study the effect of varying the conformation of the central heterocycle in the repeating unit on the Kuhn segment value of the macromolecule using such systems as models.

When studying the conformational behavior of the central quinone dihydrocycle in anthroneylidene compounds of the type **1**, the problem was posed of determining the effect of different groups at the exocyclic C=C bond on the flexibility and equilibrium conformation of molecules **1–6**. The substituents R considered in this work were varied over a wide range from strong electron donors (NMe_2) to strong electron acceptors (NO_2).



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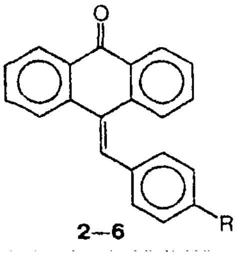

2–6

R = NO_2 (**2**), H (**3**), Cl (**4**), NMe_2 (**5**), OMe (**6**)

Calculation procedure

The geometry of the molecules of **1–6** was optimized by the semiempirical AM1 quantum-chemical method.[12] The conformational behavior of dihydrocycles in molecules **1–6** was studied by scanning the C(Ar)—C(Ar)—C(=C)—C(Ar) torsion

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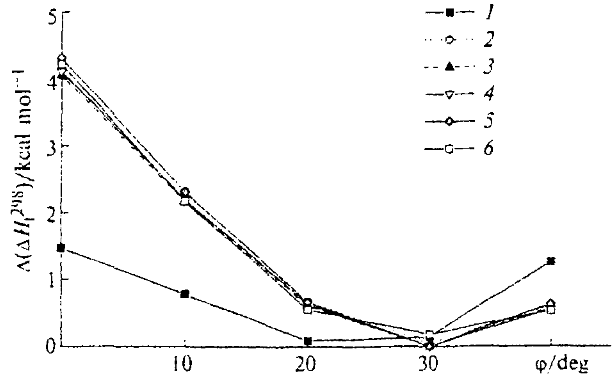
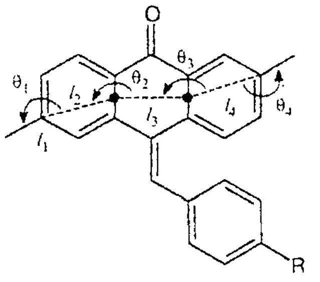


Fig. 1. Dependences of the relative heats of formation of molecules **1—6** ($\Delta(\Delta H_f^{298})$) on the bending angle of the dihydrocycle (φ). The numbering of the curves corresponds to that of the compounds.

angle (φ) in the range from +40° to −40° with an increment of 10° and full optimization of the remaining geometric parameters of the molecules (Fig. 1). Four distances and four angles are required to describe changes in the dihydrocycle geometry (Scheme 1).

Scheme 1

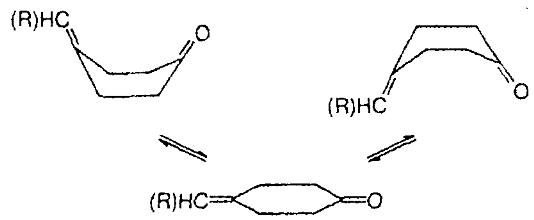


Results and Discussion

The molecular structures of compounds **2—6** were established earlier by X-ray analysis.[13] Comparison of the results of AM1 calculations of these molecules with the reported data[13] showed that the main bond lengths and bond angles are in good agreement, which justifies the use of the method for this type of molecular systems. Both methods indicate that unfavorable nonvalent interactions between the atoms of the *p*-R—C_6H_4 and *peri*-H substituents in the molecules of derivatives **2—6** cause rotation of the benzene rings in the *p*-R—C_6H_4 fragments about the C=C bond (the corresponding torsion angles are ~50°) and a twisting of this bond (the torsion angles, φ, in molecules **2—6** are ~10°). As a result, electronic effects of substituent R cannot substantially affect the structure of the central anthroneylidene fragment.

In all the molecules, the quinone dihydrocycle has an equilibrium asymmetric boat conformation, which is in agreement with both theoretical[11,13] and experimental data.[13,14] Therefore, the quinone dihydrocycle in the molecules of anthroneylidene compounds can adopt two equivalent equilibrium conformations which can undergo interconversion upon overcoming the potential barrier corresponding to the planar dihydrocycle (Scheme 2).

Scheme 2

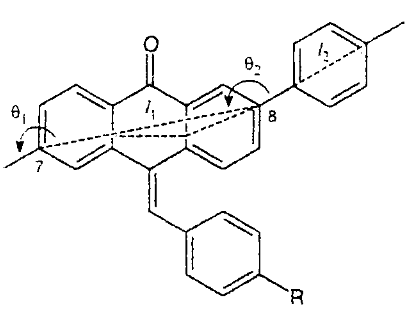


The dependences of the relative heats of formation ($\Delta(\Delta H_f^{298})$) of molecules **1—6** on the torsion angle (φ) are presented in Fig. 1. For all compounds, except for **1**, the curves are closely matched by one another and therefore it is hard to draw definite conclusions regarding the effect of the substituent on the conformational behavior of dihydrocycle.

It is known that in the case of polyheteroarylenes the Kuhn segment value, A_{fr}, which is a measure of the polymer chain rigidity, is highly sensitive to the geometry of the repeating unit of the chain.[15] Therefore, it can be used to establish which of the substituents has the greatest effect on the flattening of the dihydrocycle.[16] To this end, we chose such polymers whose repeating units contained one fixed fragment (*p*-phenylene) and one varied fragment (anthroneylidenes with different substituents). In this case, the polymer rigidity is completely determined by changes in the structure of the latter. The smaller the Kuhn segment value, the more flexible the polymer and, hence, the greater the deformation of the dihydrocycle.

Since the dihydrocycle has a distorted boat conformation, the geometry of the repeating unit of the polymer can be described using two virtual bonds (l_1, l_2) and two angles (θ_1, θ_2) between them (Scheme 3). In Fig. 2, we present the dependences of the relative heats of formation $\Delta(\Delta H_f^{298})$ of molecules **1—6** with bent quinone dihydrocycle (at different φ) on the rigidity (A_{fr}) of corresponding polymers. All compounds are characterized by nonlinear dependences, which can be divided into three groups. The first group comprises compounds with the PhCl, PhOMe, and $PhNMe_2$ substituents, the second group comprises compounds with the Ph and $PhNO_2$ substituents, whereas the third group comprises only one compound, namely, a polymer based on molecule **1**.

Scheme 3



For each of these groups, the A_{fr} values virtually lie on straight lines if the φ angles are larger than those in the equilibrium structures. The curves for the compounds belonging to the second group have the largest slope. This means that introduction of the above-mentioned substituents increases the rigidity of the partially hydrogenated ring, so a larger expenditure of energy is required to flatten the cycle. It should be noted that the heterocycle does not adopt a completely planar conformation and the rigidity of the corresponding polymer does not reach the maximum value.

The Kuhn segment value, A_{fr}, varies in a narrow range from 65 to 118 Å (Table 1). The dihydrocycle in molecule **1** is the most flexible, namely, an energy expenditure of only ~1.5 kcal mol^{-1} is required to flatten this cycle.

The above-mentioned calculations were carried out assuming that the macromolecule of each polymer consists of the repeating units with the same bending angle of the dihydrocycle. However, the repeating units with different torsion angles φ are present in real polymers. Because of long separations between heterocycles, the dependence of energy on the angle φ for the polymer remains the same as that for individual quinone dihydrocycle. This makes it possible to ignore the interaction between heterocycles.

Using this simplifying assumption, it is possible to calculate the Kuhn segment value for a real polymer assuming that it consists of comonomers which have different values of the torsion angle φ and that the probability of entrance of each type of comonomers into the polymer chain is determined by the dependence of $\Delta(\Delta H_f^{298})$ on φ. In our case, the polymer consists of six comonomers, namely, five comonomers with bending angles varied in the range from 0 to 40° with an increment of 10° and one comonomer with the dihydrocycle in the equilibrium conformation.

Previously,[17] a procedure was proposed for calculating the Kuhn segment value for the copolymer consisting of two comonomers; for each of the comonomers, the probability of entrance into the polymer chain was proportional to its mole fraction in the copolymer.[17] No calculations for copolymers consisting of a larger number of different comonomers have been carried out as yet. Therefore, we have developed a new procedure for calculating the Kuhn segment value, which takes into account (i) equiprobable entrance of each comonomer into the polymer chain (A_{eq}) and (ii) the case where the probability of entrance of each comonomer into the polymer chain is determined by the Boltzmann factor (A_B).[18–20]

Let us consider the latter case in more detail. The probability (p) of entrance of each type of comonomers into the polymer chain is proportional to the energy required for bending the dihydrocycle through the angle corresponding to a particular comonomer. To calculate this probability, we interpolated the dependence of $\Delta(\Delta H_f^{298})$ on φ with an increment of 1.25° and used it to find the $p(\varphi)$ values from the following equation

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

where $Z = \sum_{\varphi} \exp \Delta H_f^{298}(\varphi)/(kT)]$ is the Boltzmann factor.

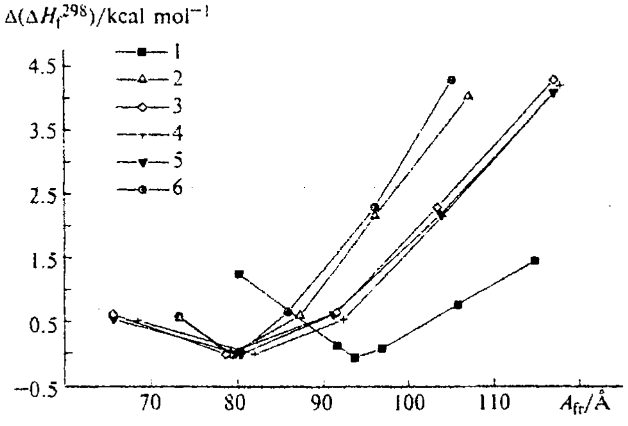


Fig. 2. Dependences of the relative heats of formation of molecules **1—6** ($\Delta(\Delta H_f^{298})$) on the Kuhn segment values (A_{fr}). The numbering of the curves corresponds to that of the compounds.

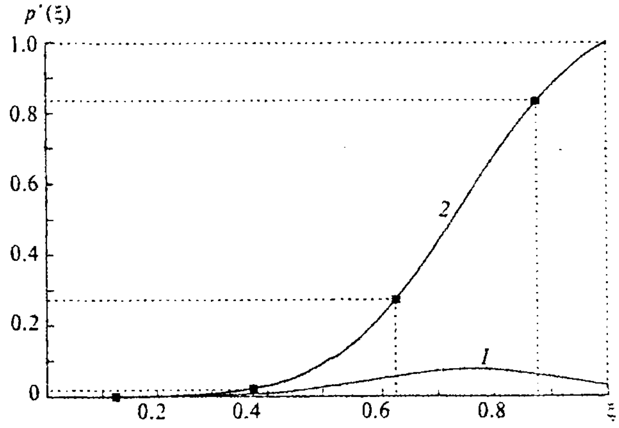
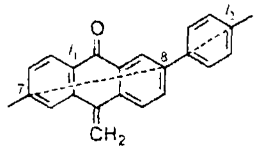
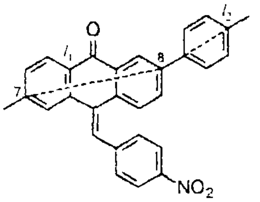
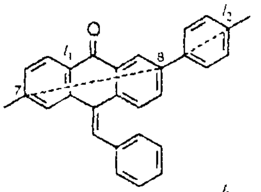
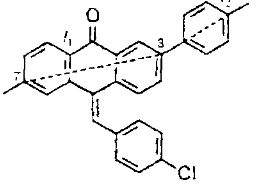
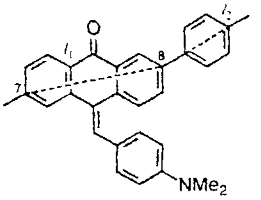
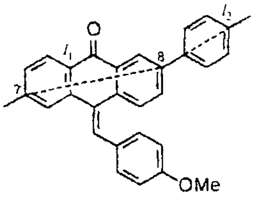


Fig. 3. Differential (*1*) and integral (*2*) probability curves of the comonomer entrance into the polymer chain.

Table 1. The energy and structural parameters of polymers based on anthroneylidene molecules **1**—**6**

Monomer	Structure	φ /deg	$\Delta(\Delta H_f^{298})$ /kcal mol^{-1}	A_{fr}	A_{eq}	A_B
				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)[a]	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)[a]	0	79.00		
		20.8(xray)[b]	—	100.81		
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)[a]	0	79.26		
		25.8(xray)[b]	—	78.46		
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)[a]	0	78.49		
		28.6(xray)[b]	—	64.75		
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)[a]	0	76.64		
		21.5(xray)[b]	—	79.31		
6		0	4.2	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)[a]	0	75.80		
		28.6(xray)[b]	—	82.80		

[a] The equilibrium structure.

[b] Data of X-ray study.

The $p(\varphi)$ curve was divided into five portions in accord with the number of torsion angles of the dihydrocycle (see above). The 0—5°, 5—15°, 15—25°, 25—35°, and 35—40° intervals corresponded to the comonomers with φ = 0°, 10°, 20°, 30°, and 40°, respectively. The angles in the range 0—40° were converted into radians and normalized to the maximum value ($0 \le \xi \le 1$). Then the $p(\varphi)$ curve was integrated between 0 and 1:

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

The $p'(\xi)$ dependence is presented in Fig. 3. On the abscissa axis, shown are the intervals corresponding to the above-mentioned intervals of variation of parameter ξ for the comonomers with the specified bending angles of dihydrocycle in the case of equiprobable entrance of comonomers into the copolymer chain. On the ordinate axis, shown are the corresponding intervals calculated taking into account the dependence of the probability on the Boltzmann factor. Since the axes were normalized to unity, these intervals can be considered as

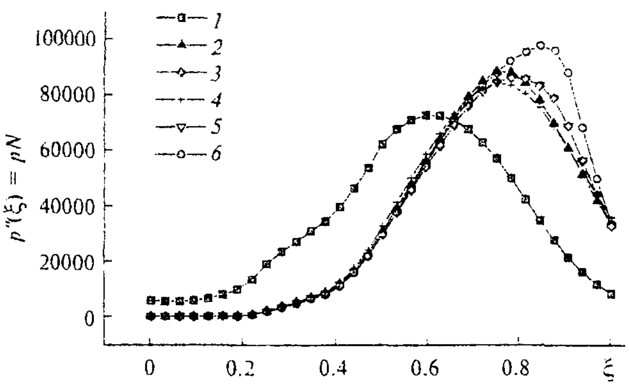


Fig. 4. Dependences of the Boltzmann factor (*N* is the total number of comonomers involved in the reaction) on the reduced bending angle of the dihydrocycle (ξ) in copolymers. The numbering of the curves corresponds to that of the compounds.

uniform distributions of random numbers in the range between 0 and 1. As can be seen in Fig. 3, the lower the dihydrocycle bending energy, the higher the probability of entrance of the comonomer with this type of cycle into the polymer chain and the wider the range of random numbers for this comonomer, and *vice versa*.

To construct the polymer chain, a random number was generated, which was uniformly distributed in the range between 0 and 1. Then, we determined the new interval of random numbers into which the previously generated random number fell and the type of comonomer which should enter into the polymer chain. In such a manner we passed from the assumption of equiprobable entrance of the comonomers into the polymer chain to the assumption that the probability of such an entrance is dependent on the energy required to change the conformation of the dihydrocycle, *i.e.*, on the Boltzmann factor.

The Kuhn segment values of six copolymers with different substituents, calculated for both the equiprobable and Boltzmann-factor-dependent entrance of the comonomers with different torsion angles of dihydrocycle into the polymer chain, are listed in Table 1. As can be seen, for all polymers, except for **1**, the A_B values are somewhat smaller than the A_{eq} values. This is in good agreement with the dependences of the Boltzmann factor on the parameter ξ for dihydrocycles with different substituents shown in Fig. 4. From this figure it can be seen that the probability of existence of comonomers with appreciably distorted angles is larger than that of flattened cycles.

For the polymer based on compound **1**, the position of maximum of the $\rho''(\xi)$ curve is nearly at the midpoint of the considered interval of variation of the torsion angle φ. Because of this, the Kuhn segment values corresponding to the equiprobable and Boltzmann distributions are close. For the polymer containing fragment **2**, the position of maximum of this curve is appreciably shifted toward strongly distorted cycles, which are characterized by the smallest Kuhn segment values. Therefore, for this polymer the Kuhn segment value calculated taking into account the Boltzmann factor is much smaller than that calculated using the "equiprobable" approach. The $\rho''(\xi)$ curves for the remaining polymers closely match one another, while the positions of their maxima lie nearly at the midpoint between the two above-mentioned maxima. Obviously, the Kuhn segment values calculated taking into account the Boltzmann factor are somewhat smaller than the corresponding "equiprobable" values.

Thus, in this work we have shown that the polymer rigidity can be varied over a wide range of the Kuhn segment values not only by varying the structure of the main polymer chain, but also by choosing appropriate substituents in the dihydrocycle.

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