Conformational flexibility of partially hydrogenated rings in the repeating units of rigid-chain heterocyclic polymers

O. V. Shishkin and I. I. Ponomarev*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085. E-mail: oleg@xray.ineos.ac.ru

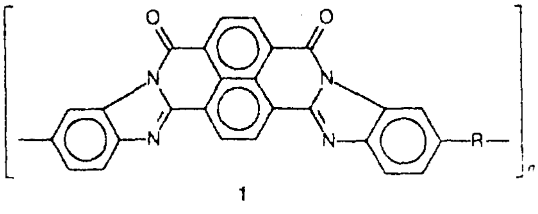
The conformational flexibility of partially hydrogenated rings in naphthylimide, naphthalic anhydride, and some of their derivatives used as model compounds for the repeating unit in rigid-chain heterocyclic polymers, was studied by the semiempirical quantum-chemical AM1 method. The partially hydrogenated rings in all of these compounds possess conformational flexibility. Transition from a planar equilibrium form to a distorted sofa conformation with a torsion angle of ±20° results in an increase in the energy of less than 1 kcal mol^{-1}. The high flexibility of partially hydrogenated rings, along with other factors, can cause finite length of the Kuhn segment in rigid-chain heterocyclic polymers.

Key words: naphthylimide, naphthalic anhydride, rigid-chain heterocyclic polymers, conformational analysis, conformational flexibility; AM1 method.

Rigid-chain heterocyclic polymers (RCHP) serve as the basis for producing high-strength, high-modulus materials and substances with nonlinear optical, photo- and conducting properties, *etc.*[1—3] The basic requirement for designing such macromolecules is their planarity and inability to change conformation. Recently, a number of RCHP (for instance,[4,5] structures **1** and **2**) with naphtylimide units and other nitrogen-containing heterocycles with no saturated carbon atoms in the main chain were synthesized. However, physicochemical studies showed that the polymeric molecules obtained have a finite length of the Kuhn segment characterizing their degree of rigidity.[6] The reasons for that phenomenon are still unclear.

Previously,[7,8] six-membered partially hydrogenated rings containing no saturated carbon atoms were shown to possess a certain conformational flexibility. Thus, transition from a planar equilibrium conformation of the ring in 6-oxo-1,6-dihydropyrimidine in a distorted sofa conformation with a =C—C(=O)—NH—C= torsion angle equal to ±20° results in an increase in the energy by less than 1.5 kcal mol^{-1} (see Ref. 8). Higher conformational flexibility was found in uracyl and thymine molecules containing a C(=O)—NH—C(=O) fragment.[7]

It is believed that the conformational flexibility of partially hydrogenated rings in RCHP monomers can cause appreciable shortening of the Kuhn segment. The conformational flexibility of model compounds **3**—**7** was studied in the AM1 approximation to verify the above assumption.



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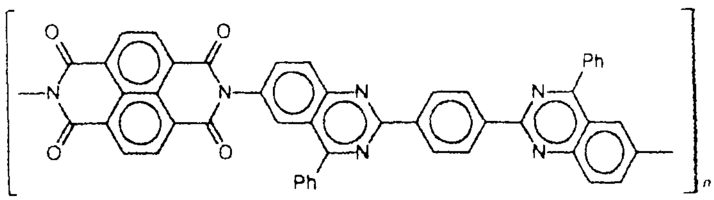

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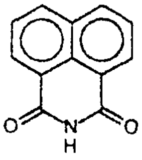

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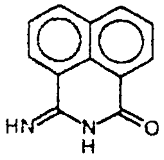

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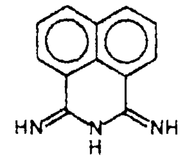

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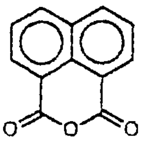

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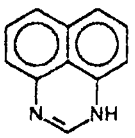

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Method of Calculations

The equilibrium structures of molecules 3—7 were calculated by the semiempirical quantum-chemical AM1 method[9] with full geometry optimization. The conformational flexibility of dihydrocycles was studied by scanning the torsion angles (τ) C(Ar)—C(sp^2)—NH—C(sp^2) (compounds 3—5), C(Ar)—C(sp^2)—O—C(sp^2) (6), and N=C—NH—C(Ar) (7) in the ±30° interval with an increment of 5° and full optimization of the remaining geometric parameters of the molecules. The results of the calculations are presented in Table 1.

Results and Discussion

The calculated equilibrium conformations of molecules 3—7 are planar, which is in good agreement with the experimental data.[10—13] The calculations showed that the partially hydrogenated rings in the compounds in question have high conformational flexibility (see Table 1). The transition from the planar equilibrium form to the distorted sofa conformation with a torsion angle of ±20° results in an increase in the energy of the molecule of less than 1.2 kcal mol^{-1}.

As can be seen from the data in Table 1, the flexibility of the imide and anhydride rings in structures 3—6 is essentially higher than the mobility of the dihydropyrimidine ring in molecule 7. The change in the energy when the ring is bent in naphthalic anhydride 6 is less than in naphthylimide 3. Replacement of the carbonyl groups of imide 3 by exocyclic azomethine groups leads to an increase in the conformational flexibility of the heterocycle. For the molecule with *trans*-orientation of the H—N=C—NHR fragment, this effect is due to mutual repulsion between the H atoms of the imino groups and the naphthalene fragment. At the same time, the increasing conformational flexibility of the imide cycle in the case of *cis*-orientation can only be associated with electronic effects.

Table 1. Calculations of the energy change (Δ*E*) in bent rings in compounds 3—7

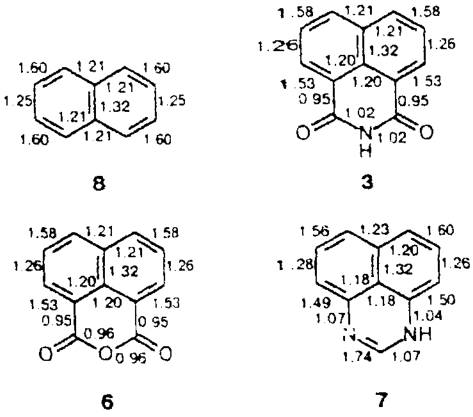
Compound	Δ*E*/kcal mol^{-1}			
	$\tau^a = 0$	$\tau = 10$	$\tau = 20$	$\tau = 30$
3	0	0.2	0.9	2.1
4^b	0	0.1	0.3	1.0
4^c	0	0.1	0.4	1.1
5^b	0	0.1	0.2	0.6
5^c	0	0.1	0.3	0.8
6	0	0.2	0.8	1.7
7	0	0.3	1.1	3.2

[a] The torsion angle (see Method of Calculations).
[b] *cis*-Orientation of the H—N=C—C(Ar) fragment.
[c] *trans*-Orientation of the H—N=C—C(Ar) fragment.

The high conformational flexibility of compounds 3—6 is of particular interest. It was shown previously[9] that the nonaromatic and antiaromatic nature of the cyclic π-system stabilizes the nonplanar conformation of a partially hydrogenated ring. In the compounds under study, the conjugated system contains 14 π-electrons and is formally aromatic. In such a case, a decrease in the polarity of the exocyclic double bond must result in an increase in the heterocycle rigidity. However, the data in Table 1 show an inverse dependence. The results obtained can be explained by steric repulsion between the electrons of the lone electron pair of the O or N atom of the exocyclic double bond and the adjacent H atom of the naphthalene fragment. The increase in the length of the C=NH bond compared to that of the C=O bond results in shortening of the distance between these atoms and, as a sequence, to increasing repulsion.

There are no such unfavorable nonvalent interactions in molecule 7, which has an aromatic (14 π-electrons) conjugated system as well. Nevertheless, the dihydropyrimidine ring is conformationally flexible even in this case. Hence, the steric effects of the substituents favor an increase in the conformational flexibility of the partially hydrogenated ring, but are not determining factors. A comparison of the calculated bond orders (*P*) in molecules 3, 6, 7, and in naphthalene 8 (Scheme 1) showed that annelation of an aromatic bicycle by imide, anhydride or 1,2-dihydropyrimidine rings does not result in an appreciable change in the *P* values in the naphthalene fragment. Based on these facts, we can

Scheme 1



assume that the conjugation between the aromatic bicycle and the annelated cycle is rather weak. This allows one to distinguish two weakly related conjugated systems in molecules 3—7 — the aromatic system of the naphthalene fragment (10 π-electrons) and the nonaromatic system of the imide, anhydride, and 1,2-dihydropyrimidine cycles (7 π-electrons).

Thus, as in other partially hydrogenated heterocycles containing no saturated carbon atoms,[9] the conformational flexibility in compounds 3—7 is due to the nonaromatic nature of the cyclic π-system. The increase in flexibility of the anhydride ring compared to the flexibility of the imide ring can likely be explained by a lower participation of the lone electron pair of the oxygen atom in conjugation compared to that of the N atom.

The results obtained allow us to assume that the conformational non-rigidity of the partially hydrogenated heterocycles constituting the RCHP substantially affects deformation of the rod-like macromolecule and can result in a decrease in the Kuhn segment values that determine the basic properties of the polymers and materials for which they serve as the basis.

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