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Theoretical study of *N*-(*o*-aminophenyl amic) acid cyclodehydration to 1,2-benzoilenebenzimidazole as a model reaction of ladder polypyrrones synthesis: thermodynamic and thermochemical data

Roberto Salcedo*, Leticia Valle, Larissa Alexandrova, Dmitri Likhatchev

II-UNAM, Apdo. Postal 70-360, 04510 Deleg. Coyoacan, Mexico

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Abstract

The mechanism of polyimidazopyrrolones formation was studied via thermodynamic simulation of *N*-(*o*-aminophenyl)amic acid cyclodehydration to 1,2-benzoylenebezimidazole. It was found that 2-(*o*-carboxyphenyl)benzimidazole and *N*-(*o*-aminophenyl)phthalimide were the most thermodynamically favorable intermediates of this process. The thermodynamic possibility of 1,2-benzoylenebezimidazole formation from *N*-(*o*-acetamidophenyl)phthalimide and *N*-(*o*-trifluoroacetamidophenyl)isophthalimide was also evaluated using the same method. All thermodynamic values were obtained from semiempirical quantum mechanics calculations.

Keywords: Polyimidazopyrrolones; Thermodynamic simulation; Model reaction

1. Introduction

Ladder polyimidazopyrrolones, commonly referred to as polypyrrones, are attracting increasing attention as promising materials for new technologies. The planar geometry of fused aromatic and heterocyclic rings of these polymers appears to be the perfect for π conjugation, and gives rise to interesting electrical, electronic and nonlinear optical properties [1–3]. In combination with the excellent environmental stability, thermal and chemical resistance, as well as good mechanical characteristics, this could make polypyrrones very desirable for device applications.

However, additional effort is required to improve processability and final functionality of these polymers. The methods of their synthesis were developed in the mid-1960s after computer simulation of polymer chain degradation based on a random bond-breakage mechanism predicted extremely high thermal stability of polypyrrones [4,5]. However, experimental data confirmed this theory only partially. The thermal resistance of polypyrrones were found to be controlled to a great extent by weaker residual precursor units, and did not exceed significantly corresponding characteristics of single chain polyheteroarylenes [6].

These defective units result from incomplete cyclodehydration that is complicated by kinetic interruption effect [7], decarboxylation [8] and other chemical decomposition reactions [9] very possible under the severe conditions of high-temperature curing. This problem has not yet been effectively

* Corresponding author.

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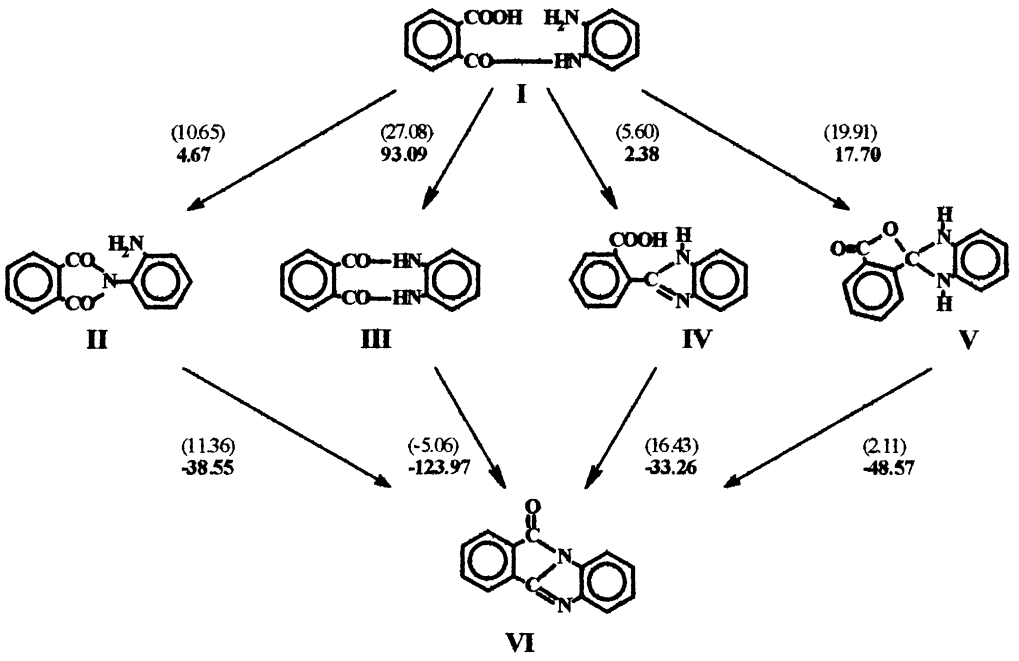


Scheme 1. Thermal cyclodehydration of *N*-(*o*-aminophenyl)phthalamic acid (the values in parenthesis correspond to 300 K, and those in bold type to 400 K).

resolved by using the known synthesis methods: neither one-step high-temperature polycondensation of aromatic tetra-amines with dianhydrides of tetracarboxylic acids (or their derivatives) in polyphosporous acid or a multistep procedure via preparation of soluble precursors followed by their thermal cyclodehydration in condensed state.

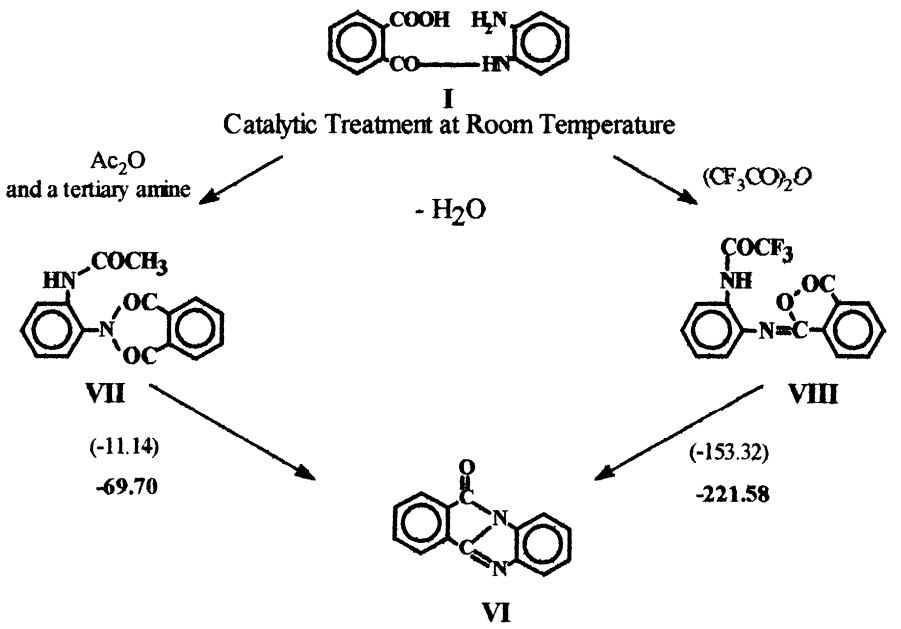
The reaction schemes of both these routes to polypyrrones are quite complicated [6]. No final agreement has yet been reached in the literature over their principal pathways, main intermediates and possible side reactions. In the present work, this problem was studied by using semiempirical quantum and molecular mechanics methods included into the CERIUS software package for thermodynamic simulation of the model reaction of *N*-(*o*-aminophenyl)phthalamic acid conversion to 1,2-benzoylenebezimidazole (structures **I** and **VI** in Scheme 1, respectively). The thermodynamic possibility of 1,2-benzoylenebezimidazole formation from *N*-(*o*-acetamidophenyl)phthalimide and *N*-(*o*-trifluoroacetamidophenyl)isophthalimide (compounds **VII** and **VIII** in Scheme 2) was also evaluated using the same method.

In this work, we carried out thermodynamic and thermochemical study in order to elucidate the processes involved in the processes involved in the reaction. Calculation of energetic barriers would be useful and will be considered in a future work.

2. Methodology

All calculations were performed using the AM1 [10] (Austin model 1) method from MOPAC software [11] included in the Cerius package[1] with total optimization of the geometry using the BFGS algorithm and proving the absolute minima with the EF (eigenvector following). The thermodynamic data (ΔS and ΔH) were obtained from a frequencies calculation on the optimized and minimum gradient structure in each case. Initial geometries were obtained by the universal molecular mechanics method [12] from the same software package. The values for free energy of the compounds (ΔG) were calculated from the equation:

[1] The results published were generated using the program CERIUS2TM, developed by Molecular Simulations Inc.



Scheme 2. Cyclization of *N*-(*o*-acetamidophenl)phthalimide and *N*-(*o*-trifluoroacetamidophenyl)isophthalmide (the values in parenthesis correspond to 300 K, and those in bold type to 400 K).

$\Delta G = \Delta H - T\Delta S$. The formation entropy values were obtained from the subtraction of absolute entropy results obtained from the MOPAC calculations and the data corresponding to the absolute entropy for the elements [13].

AM1 method has been demonstrated to be very reliable in thermochemical calculations [14] and this fact is strengthened with good results obtained for water, as shown before.

3. Results and discussion

The mechanism of *N*-(*o*-aminophenyl)phthalamic acid conversion to 1,2-benzoilenebezimidazole was extensively studied by numerous research groups [7,8,15–18]. In accordance to the controversial experimental data, the opinions over the principal intermediates of this reaction have split in favor of *N*-(*o*-aminophenyl)phthalimide [15], 2-(*o*-carboxyphenyl)benzimidazole [18,19] (structures **II** and **IV** in Scheme 1, respectively), or both of them [17,20]. In addition, Dawans and Marvel [20] proposed that primary cyclodehydration of **I** could also lead to the formation of the eight-membered cyclic diamide (**III** in Scheme 1) that may exist in equilibrium with the amino-imide **II**, as well as Paudler and Zeiler [19] who pointed out that this reaction might also result in a lacton structure (**V** in Scheme 1). The reaction scheme summarizing all these experimental data and proposals is presented in Scheme 1.

The obtained thermodynamic data at 300 K are given in Table 1 (in parenthesis), whereas the corresponding values of the reaction free energy are shown in Scheme 1. The free energy of formation of water, ΔG_f, calculated by the same method, at this temperature yielded a result of $-$ 56.049 kcal/mol that is in agreement with the reported data [13].

The total free energy for the cyclodehydration of **I** to **VI** had a value of 22.021 kcal/mol at 300 K, and corresponding equilibrium constraint K_p was 9.037×10^{-17}. Thus, this reaction has to be thermodynamically ineffective at this temperature. At 400 K, ΔG turned to the negative value of $-$ 30.876 kcal/mol and the K_p increased to 7.435×10^{16}. The free energy of formation of water at this temperature was equal to $-$ 55.110 kcal/mol. The thermodynamic parameters at 400 K are summarized in Table 1, while ΔG values of the reactions are shown in Scheme 1.

It can be seen that the changes of the free energy for

Table 1
Thermodynamic data at 300 and 400 K

Compound	ΔH (kcal/mol)	ΔS (kcal/mol)	ΔG (kcal/mol)
I	− 59.08	− 173	10.00
	(− 66.25)	(− 193)	(− 8.28)
II	18.97	− 135	72.79
	(12.58)	(− 153)	(58.42)
III	34.85	− 136	158.82
	(28.68)	(− 154)	(53.36)
IV	14.95	− 131	67.50
	(8.59)	(− 149)	(53.36)
V	25.78	− 143	82.81
	(19.65)	(− 160)	(67.68)
VI	34.85	− 136	89.35
	(93.20)	(− 109)	(125.84)

Data at 300 K are shown in parenthesis.

the primary cyclodehydration remained positive, even at this temperature. However, a significant decrease was obtained at 300 K. The lowest values of 2.38 and 4.67 kcal/mol were found for the pathways from **I** to **IV** and **II**, respectively. Thus, these appear to be the most thermodynamically preferable intermediates in the stepwise cyclodehydration of **I** at temperatures around 400 K. This consideration is in agreement with the experimental data. The formation of **II** and/or **IV** during thermal treatment of **I** at 410–430 K was registered in numerous studies [17,20] and both of them were separated as stable individual compounds.

In contrast to these, structures **III** and **VI** have never been neither isolated as individual compounds nor reliably detected as intermediate products during the formation of **VII** via thermal treatment of *N*-(*o*-aminophenyl)phthalamic acid **I** [17,21]. This fact is consistent with the high values of ΔG obtained for these structures in the present study at 400 K: 93.09 and 17.70 kcal/mol for **III** and **VI**, respectively. The equilibrium amounts of the these high-energy components are expected to become vanishingly small, yet they may be still reactive intermediates affecting the reaction scheme [22].

Positive ΔG values were obtained for the secondary dehydration of the structures **II**, **IV**, **V** at 300 K, but became quiet low negative values for all possible intermediates **II**–**V** at 400 K (see Scheme 1). Thus, the formation of the ending product **VI** could be considered as a thermodynamically favorable reaction at elevated temperatures. The gain in the free energy on this step was sufficient for compensating the positive values of ΔG found for the primary cyclodehydration of I, thus making conversion to **VI** thermodynamically beneficial in total.

It was of particular interest to evaluate a thermodynamic possibility of 1,2-benzoylenebenzimidazole **VI** formation from *N*-(*o*-acetamidophenyl)phthalimide or *N*-(*o*-trifluoroacetamidophenyl)isophthalimide (**VII** and **VIII** in Scheme 2).

It could be expected that these structures may be obtained selectively by a catalytic treatment of the amino acid **I** at room temperature by the mixture of acetic anhydride and a tertiary amine or by trifluoroacetic anhydride, respectively. The efficiency of this approach was proven for the hydroxy polyimides based on 2,2-bis(3-amino-hydroxyphenyl)-hexafluoro-propane [23].

Chemical imidization of the correspondent precursor poly(amic acid) in the mixture of acetic anhydride and pyridine was found to be accompanied by an esterification of the OH groups in the diamine moieties. The resulting acetate groups exhibited higher reactivity toward imide cycle with respect to the original hydroxyls. The imide-to-benzoxazole rearrangement, caused by the reaction of the ortho positioned substituent with imide cycle, occurred at 60–70 K lower temperatures for the esterified polyimides [23].

The values of ΔG for the cyclodehydration of **VII** and **VIII** at 400 K are shown in Scheme 2. They were obtained negative even at 300 K and significantly lower than the similar parameters for the compounds **II**–**V**. The lowest value was calculated for the cyclization of **VII**. The free energy of the formation of acetic acid resulting from these transformations made up −104.24 kcal/mol at 300 K and −103.25 kcal/mol at 400 K; and trifluoroacetic acid −225.43 kcal/mol at 300 K and −220.09 kcal/mol at 400 K. The obtained results indicate that from point of view thermodynamic both **VII** and **VIII** are very promising materials for conversion to 1,2-benzoylenebezimidazole **VI**. However, in practice, energetic barriers of these transformations will play the main role.

4. Conclusions

The thermodynamic simulation of *N*-(*o*-aminophenyl)amic acid cyclodehydration to 1,2-benzoylenebezimidazole as a model reaction for polypyrrones

synthesis demonstrated that 2-(*o*-carboxyphenyl) benzimidazole and *N*-(*o*-aminophenyl)phthalimide were the most thermodynamically favorable intermediates of this complicated process. It was found that from point of view of thermodynamic 1,2-benzoylenebezimidazole could be easily obtained from *N*-(*o*-acetamidophenyl)phthalimide or *N*-(*o*-trifluoroacetamidophenyl)isophthalimide.

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