Intramolecular Hydrogen Bonding and Electronic Structure of Thiadiazole Annulated Hemihexaphyrine

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Dedicated to Professor Oleg Aleksandrovich Golubchikov on the occasion of his 70-th birthday

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Different tautomeric structures of thiadiazole annelated hemihexaphyrine (TDAHHp) were considered using DFT in B3LYP/pcseg-2 approximation. Energetics of the intramolecular hydrogen bonding was quantitatively estimated by means of NBO and AIM calculations and according to the NBO analysis results, the most energetically favorable tautomer of TDAHHp surprisingly turned out to possess the lowest total H-bond stabilization energy. The results are compared with that for the previously studied hemihexaphyrine – 2,3,5,10,12,13,15,20,22,23,25,30-dodecaaza-hexaphyrin (C_{30}H_{15}N_{15}S_{3}). Electronic absorption and infrared spectra were simulated for the most favorable tautomer of TDAHHp.

Keywords: Hemihexaphyrine, hydrogen bond, electronic spectrum, NBO, AIM.

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Статья

Porphyrazines

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Внутримолекулярные водородные связи и электронное строение тиадиазол–аннелированного гемигексафиразина

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С помощью DFT расчетов в приближении B3LYP/pcseg-2 изучены семь таутомеров тиадиазол-аннелированного гемигексафиразина (TDAHHp). Энергия внутримолекулярных водородных связей в таутомерах оценивалась с использованием двух различных подходов: NBO анализ распределения электронной плотности и топологической теории AIM. На основе результатов NBO-расчетов сделано неожиданное заключение о том, что наиболее энергетически выгодный таутомер TDAHHp характеризуется минимальной суммарной энергией внутримолекулярных водородных связей. Результаты расчетов сопоставлены с результатами ранее изученного гемигексафиразина – 2,3,5,10,12,13,15,20,22,23,25,30-додекаaza-hexaphyrin (C_{30}H_{15}N_{15}S_{3}). Для наиболее энергетически предпочитительного таутомера TDAHHp проведены TDDFT расчеты электронных переходов. Смоделирован инфракрасный спектр исследуемого соединения на основе квантово-химических расчетов.

Ключевые слова: Гемигексафиразин, водородная связь, электронный спектр поглощения, NBO, AIM.
Introduction

Investigations of the molecular structure and tautomeric behaviour of macroheterocyclic systems have been the subject of the many recent studies.\(^{(1-6)}\) Commonly used DFT calculations often allow to establish the most energetically favorable tautomer and then the preference is discussed in light of fundamental concepts of chemistry. Intramolecular hydrogen bonding is one of the most important issues among them for such objects. However, it is essential to put general considerations on the quantitative basis. One of the most popular approaches for quantitative estimation of the phenomenon of hydrogen bonding nowadays was developed in AIM theory and it is focused on the locating so-called "bond critical points" (BCPs) corresponding to hydrogen bonds. Besides, in the recent study of Vogt et al.,\(^{(7)}\) the energy of a weak hydrogen bond was estimated based on the results of the NBO analysis.

Results and Discussion

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NH-Tautomerism and energetics of the intramolecular hydrogen bonding

According to the results of the calculations, none of the optimized planar structures of the tautomers possesses imaginary frequencies, except for tautomer 1PT-2, in which strong repulsion between the neighboring H atoms appears in the planar framework. Equilibrium structures of all six NH-tautomers are much higher in energy than the parent TDAHHp structure (see Table 1).

The lowest in energy parent TDAHHp structure contains six Nt…H contacts (or three three-centered contacts Nt…H…N). If one contact becomes broken due to "migration" of a hydrogen (TDAHHp→1PT-1), the energy of the whole molecule increases by 39.2 kJ mol\(^{-1}\) (see Table 1). Further migration of another H atom (1PT-1→2PT-3) again leads to significant increase of energy.

The dependence of the relative energy of the most favorable NH-tautomers on the number of intramolecular H-bonds is almost linear (see Figure 2). It is possible to calculate the energy difference per one broken hydrogen bond (which should be approximately equal to the H-bond energy) by dividing the relative energy \(\Delta E\) by the differ-

\[
\Delta E, \text{kJ mol}^{-1}
\]
ence in the number of H-bonds between corresponding tautomers. For example, in the case of 1PT-1, this value is 39.2/(6–5)=39.2 kJ·mol⁻¹.

One can estimate the energy of the intramolecular hydrogen bonding from the results of the NBO analysis. In terms of the orbital interactions, they can be treated as donor-acceptor interactions between the lone pair (LP) of the Nₜ atom and σ*(N-H) antibonding orbital. The D₃h-TDAHHp structure might have been considered to correspond to the minimum due to the largest number of the intramolecular Nₜ…H contacts. However, the results of the NBO calculations distinctly demonstrate the opposite trend within the set of the most favorable models (1PT-1, 2PT-3 and 3PT). Much shorter Nₜ…H contacts in these structures (ca. 1.95) as compared to the parent TDAH Hp structure (ca. 2.20) stabilize the whole molecule in a greater degree (see Table 1). So, the formal largest number of Nₜ…H contacts apparently is not the reason of the pronounced stabilization of the D₃h-TDAH Hp structure. Note, that the migration of the inner hydrogen atoms leads to significant changes in the bond lengths and angles in the macrocycle (see Figure S1).

Another possible way to assess the energy of a hydrogen bond (E_HB) is an approach developed by E. Espinosa et al.[18] in the framework of AIM theory. They proposed an equation, connecting this energy with the potential energy density V(r_Cp) calculated at a critical point: E_HB = 0.5V(r_Cp). We found the bond critical points (BCPs) corresponding to hydrogen bonds in the most favorable tautomers, calculated the values of E_HB according to the above-mentioned formula, and estimated the total energy of intramolecular hydrogen bonds E_{H_B, total} (see Table 1). Interestingly, the trend in E_HB is opposite to that calculated using NBO approach (see Figure 3). AIM calculations underestimate the energies of short Nₜ…H contacts in the structures 1PT-1, 2PT-3 and 3PT as compared to the results of the NBO analysis and do not identify BCPs for the long-range Nₜ…H interactions (see Table S1). Despite the overall increasing tendency, small differences between the values of E_HB for the tautomers as compared to ΔE (Table 1) cannot act as a main reason for stabilization of the parent TDAH Hp structure.

Electronic absorption spectrum

Calculations of the electronic absorption spectrum (Figure 5) predict the most intensive peak with oscillator strength of f=0.68 to correspond to the excitation to the lowest 1E¹ state originating from HOMO→LUMO (2e''→1e*') transition. The next intensive peak at λ=336 nm corresponds to transition 1a''→1e*'. Detailed data are given in Table 2. The MO level diagram for TDAH Hp is shown in Figure 6 and the energies of the MOs are given in Table S2.

IR Spectrum

TDAH Hp molecule possesses 138 normal modes of vibration. The vibrational representation for TDAH Hp in D₃h symmetry is Γ=16A¹'+15A²'+31E¹'+6A''₁'+9A''₂'+15E''. Assignment of the infrared active modes was carried out by the potential energy distribution (PED) analysis among internal coordinates using the VibModule program.[19] The N–H stretching vibration is predicted at 3444 cm⁻¹ (E'). The peak at ω=787 cm⁻¹ can be assigned to the movement of hydrogen atoms out of the plane of the macrocycle (A''₂). It should be noted that the composition of most vibrational modes is complicated. Thus, the mode at ω=1242 cm⁻¹ (E') corresponds to the stretching of Sₜ-Ct (contribution ~15 %), Nₚ-C (−12%), Nₚ-C (−23%) bonds and in-plane bending of N-H (−15%). The vibration mode at ω=1444 cm⁻¹ (E') corresponds mostly to the stretching of Cα-Nₚ (~30 %) and C-Nₚ (~30%) bonds. The main contribution (~70 %) to the modes at 1680 cm⁻¹ (E') and 1686 cm⁻¹ (E') stems from the stretching of C-Nₚ bond. Note, that the region from 1800 to 3400 cm⁻¹ contains no peaks.

Conclusions

The tautomeric behaviour of thiadiazole annelated hemihexaphyrazine (TDAH Hp) was studied for the first time by means of DFT calculations. The parent TDAH Hp
Figure 4. Models of possible tautomers of TDAHHp.
structure corresponds to the minimum of energy, while the other NH-tautomers are much (39.2 kJ·mol⁻¹ and more) higher in energy. Thus, the conformational behaviour of **TDAHHp** exhibits both qualitative and quantitative similarity with that of the previously studied C₃₀H₁₅N₁₅S₃ macrocycle. However, NBO and AIM calculations performed in the present study provide another point of view on the pronounced stability of the main D₃h-structure of **TDAHHp** as compared to those short N...H bonds in the tautomers stabilize the whole structure in a greater degree as compared to six long Nt...H contacts in the parent **TDAHHp** structure. AIM calculations demonstrate the opposite trend in changing of the total hydrogen bonding energy within the series of the tautomers, but nevertheless, the differences between the values of E_{HB,total} are about 10 times less as compared to the corresponding ΔE magnitudes. Therefore, intramolecular hydrogen bonding is not an interaction stabilizing the main D₃h-structure of **TDAHHp** as might have been thought from qualitative point of view. Investigations of the similar macroheterocyclic systems can shed further light on the true reason of tautomeric preference.

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**Table 2.** Calculated composition of the lowest excited E' states, excitation energies and oscillator strengths for **TDAHHp**.

| State | Composition (%) | Excitation energy | Oscillator strength |
|-------|-----------------|-------------------|---------------------|
|       |                 | E, eV             | λ_{calc}, nm        | f^0                |
| 1E'   | 2e''→1e''* (96) | 2.9              | 424                | 0.68               |
| 2E'   | 2e''→1a₁''* (84) | 3.3              | 380                | 0.12               |
|       | 2e''→2e''* (10) |                  |                    |                    |
| 4E'   | 1a₁''→1e''* (7)  | 3.5              | 349                | 0.17               |
|       | 2e''→1a₁''* (68) |                  |                    |                    |
|       | 2e''→2e''* (19) |                  |                    |                    |
| 5E'   | 1a₁''→1e''* (87) | 3.7              | 336                | 0.44               |
| 6E'   | 1e''→1e''* (33)  | 4.0              | 312                | 0.06               |
|       | 1a₂''→1e''* (39) |                  |                    |                    |
|       | 2a₁''→1e''* (20) |                  |                    |                    |
| 7E'   | 1e''→1e''* (14)  | 4.1              | 305                | 0.19               |
|       | 1a₂''→1e''* (7)  |                  |                    |                    |
|       | 2a₂''→1e''* (70) |                  |                    |                    |
| 12E'  | 1e''→1a₁''* (28) | 4.9              | 254                | 0.34               |
|       | 1a₂''→2e''* (6)  |                  |                    |                    |
|       | 2e''→2a₁''* (43) |                  |                    |                    |

*Only the excited states with an oscillator strength larger than 0.05 are reported.*
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