Supporting information for the article:

Intramolecular Hydrogen Bonding and Electronic Structure of Thiadiazoleannelated Hemihexaphyrazine

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

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Content:

Optimized Cartesian coordinates for the tautomers of TDAHHp at B3LYP/pcseg-2 level:
TDAHHp

7	5.647323000	4.716202000	0.000000000
7	1.260689000	-7.248826000	0.000000000
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7	6.908012000	2.532624000	0.000000000
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6	4.625173000	1.320215000	0.000000000
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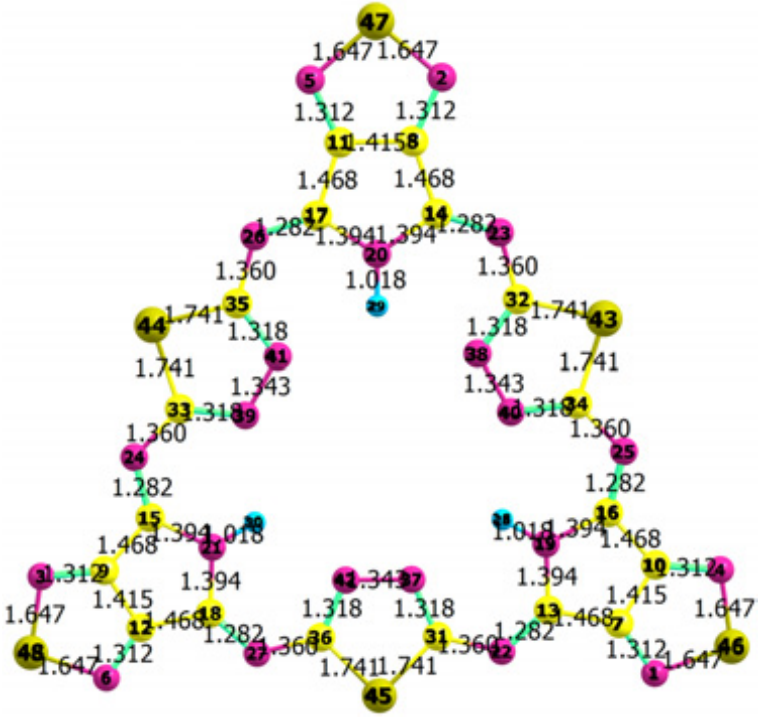
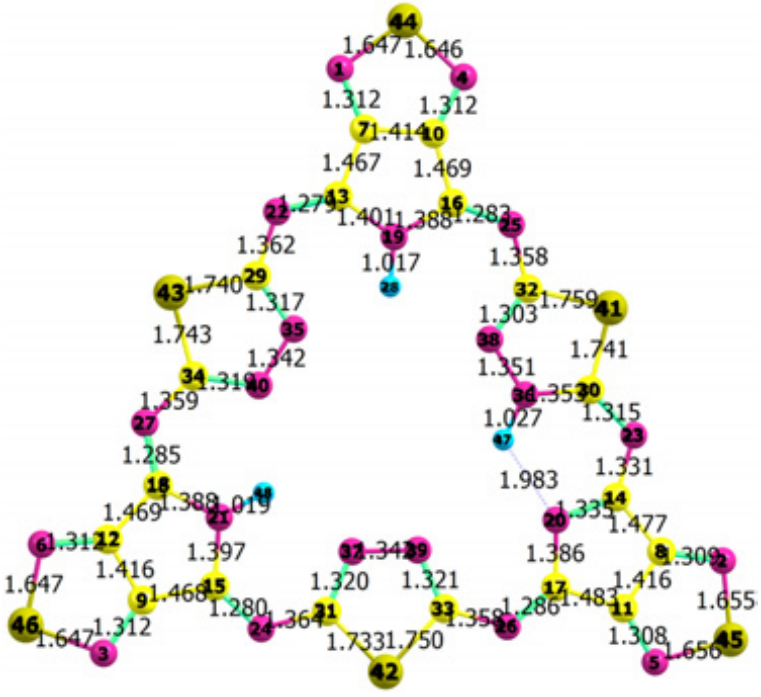
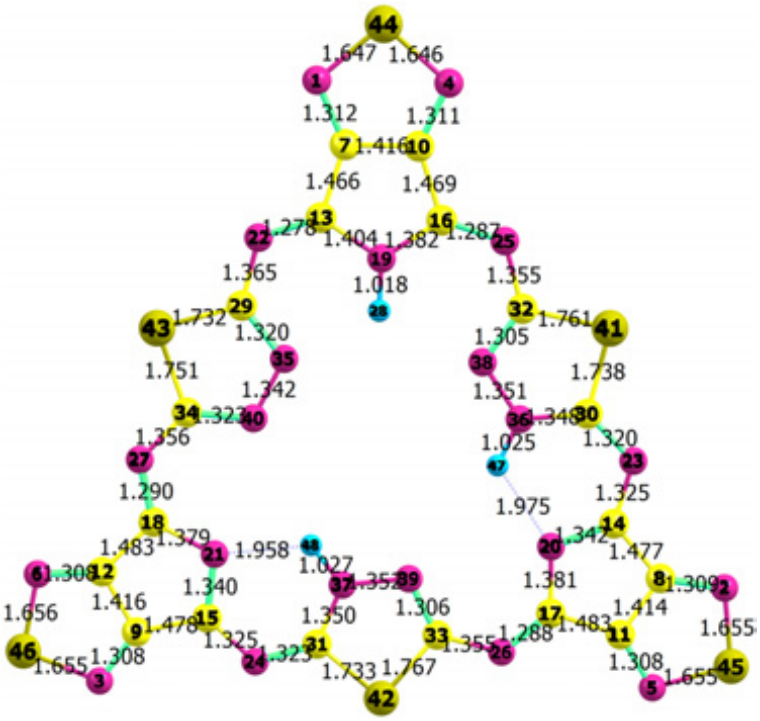


TDAHHp



1PT-1



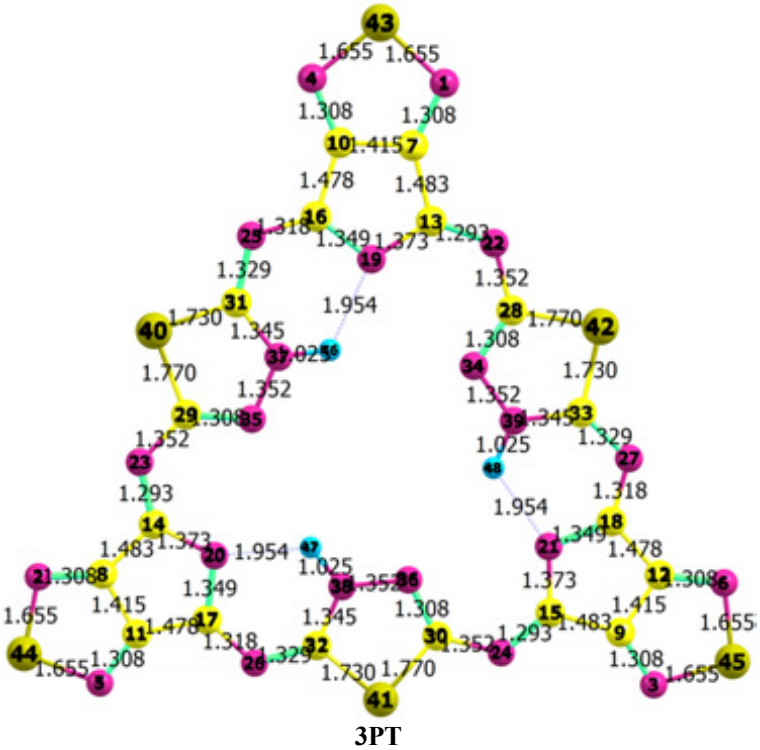


Figure S1. Comparison of the bond lengths in the most energetically favorable tautomers of **TDAHHp**.

Table S1. Energies of the donor-acceptor interactions of the type LP(N)→σ*(N-H) extracted from the results of the NBO analysis and corresponding values of EHB determined from AIM calculations.

TDAHHp

$E_{sum}^{(2)}$, kcal mol^{-1}	$E_{HB, total}$, kcal mol^{-1}
6*3.69 = **22.14**	6*4.29 = 25.74

1PT-1

Donor	Acceptor	$E^{(2)}$, kcal mol^{-1}	E_{HB}, kcal mol^{-1}
162. LP (1) N 37	/***. BD*(1) N 21 - H 48	4.73	4.83
165. LP (1) N 40	/***. BD*(1) N 21 - H 48	4.02	4.54
152. LP (1) N 20	/***. BD*(1) N 36 - H 47	9.05	7.44
163. LP (1) N 38	/***. BD*(1) N 36 - H 47	0.73	-
163. LP (1) N 38	/***. BD*(1) N 19 - H 28	2.12	3.24
160. LP (1) N 35	/***. BD*(1) N 19 - H 28	4.72	4.94
		25.37	**24.99**

2PT-3

Donor	Acceptor	$E^{(2)}$, kcal mol^{-1}	E_{HB}, kcal mol^{-1}
160. LP (1) N 35	/***. BD*(1) N 19 - H 28	5.91	5.46
163. LP (1) N 38	/***. BD*(1) N 19 - H 28	2.61	3.65
152. LP (1) N 20	/***. BD*(1) N 36 - H 47	9.43	7.55
163. LP (1) N 38	/***. BD*(1) N 36 - H 47	0.76	-
153. LP (1) N 21	/***. BD*(1) N 37 - H 48	10.06	7.92
164. LP (1) N 39	/***. BD*(1) N 37 - H 48	0.71	-
165. LP (1) N 40	/***. BD*(1) N 37 - H 48	0.52	-
		30.00	**24.58**

3PT

Donor	Acceptor	$E^{(2)}$, kcal mol^{-1}	E_{HB}, kcal mol^{-1}
151. LP (1) N 19	/***. BD*(1) N 37 - H 46	10.33	7.97
164. LP (1) N 35	/***. BD*(1) N 37 - H 46	0.73	-
153. LP (1) N 20	/***. BD*(1) N 38 - H 47	10.33	7.97
165. LP (1) N 36	/***. BD*(1) N 38 - H 47	0.73	-
155. LP (1) N 21	/***. BD*(1) N 39 - H 48	10.33	7.97
163. LP (1) N 34	/***. BD*(1) N 39 - H 48	0.73	-
		33.18	**23.91**

Table S2. Symmetry and energy levels (in eV) of the highest occupied and lowest unoccupied molecular orbitals for **TDAHHp**.

MO	**TDAHHp**		
Unoccupied	sym	E, eV	Degeneracy
LUMO+4	$2a_2$''*	-1.24	1
LUMO+3	2*e*''*	-2.77	2
LUMO+2	$1a_1$''*	-2.80	1
LUMO+1	$1a_2$''*	-2.95	1
LUMO	1e''*	-3.52	2
Occupied			
HOMO	2e''	-6.65	2
HOMO-1	$1a_2$'	-7.50	1
HOMO-2	$1a_1$''	-7.54	1
HOMO-3	2e'	-7.75	2
HOMO-4	$2a_2$''	-7.87	1
HOMO-5	$1a_2$''	-8.22	1
HOMO-6	1e''	-8.23	2
HOMO-7	1e'	-8.47	2

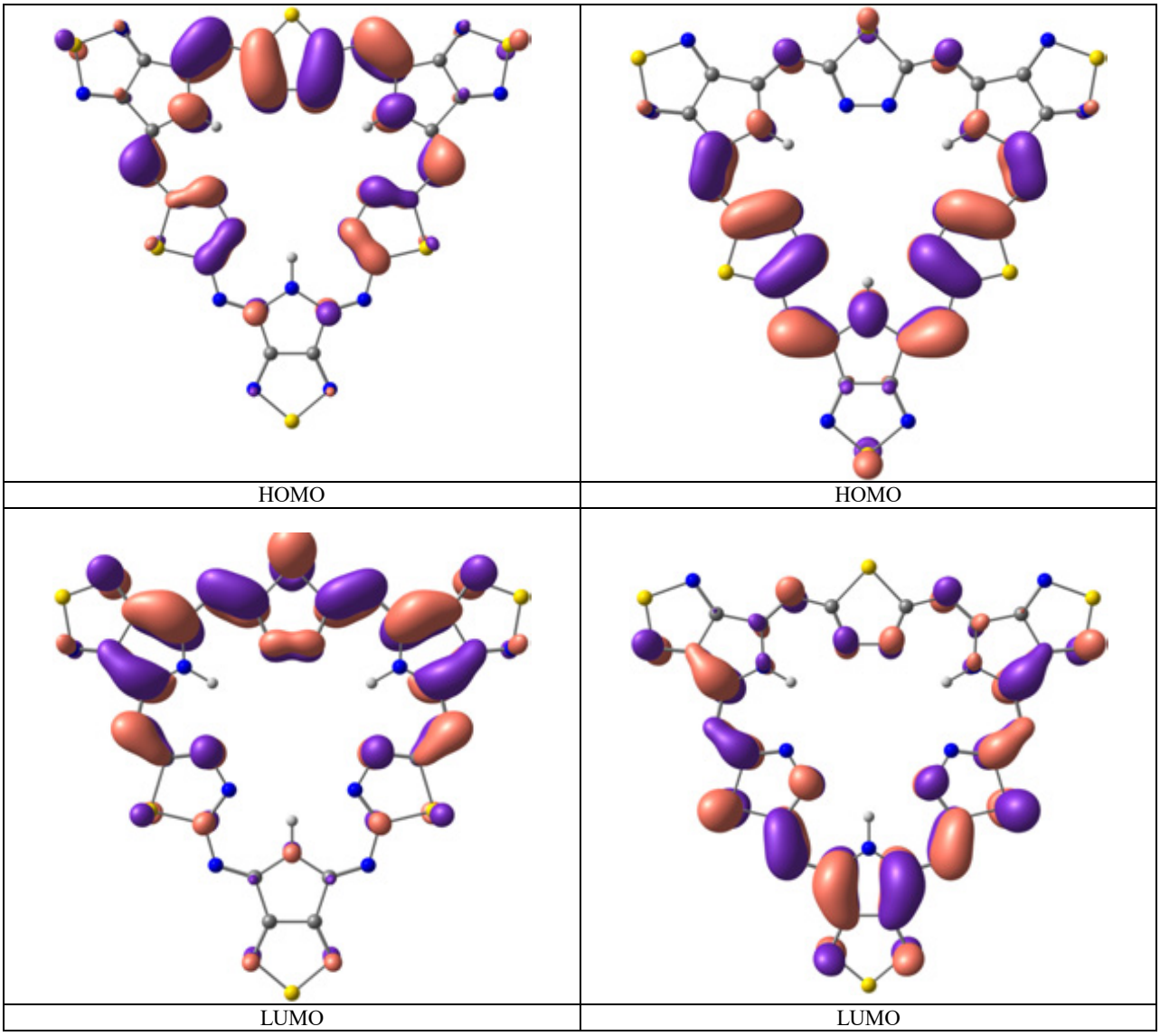


Figure S2. Frontier molecular orbitals of **TDAHHp**.