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STRUCTURE AND REACTIVITY OF URACIL DERIVATIVES. 2*. AMBIDENT NUCLEOPHILIC REACTIVITY OF 5-DIAZOURACIL

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On the basis of 3-21G type ab initio calculations we have studied all the possible complexes of 5-diazouracil with boron trifluoride. The most stable of these are the systems with the BF_3 coordinated at the 3, 9, and 10 positions of the heterocyclic molecule.

Keywords: diazo compound, donor-acceptor complex, pyrimidinedione, uracil.

A classic example of a donor-acceptor interaction is the coordination of atoms with unshared electron pairs into the vacant 2*p*-atomic orbitals of the boron atom in its trifluoride BF_3 [2]. We have previously discussed [1] the 5-diazouracil molecule which contains several, concurrent donor (nucleophilic) centers. Bearing in mind the particular role of BF_3 type electrophilic agents for the activation of diazo compounds in such reactions as azo conjugation [3, 4] we report here a study of the use of 3-21G type *ab initio* calculations of the thermodynamic stability of all possible donor-acceptor complexes of 5-diazouracil with boron trifluoride.

The calculations were carried out using a program package [5]. The geometrical parameters were optimized using the Schlegel analytical gradient method [6]. Optimization was carried out with an accuracy of 0.001 Å for bond lengths and 0.1° for angles and an SCF procedural accuracy of 10^{-9} for matrix density and RMS intensity 10^{-4} a.u. The frequencies of harmonic vibrations and ZPE energy were calculated analytically with the use of second derivatives.

Through carrying out the calculations on the potential energy surface (PES) of the system 5-diazouracil$\rightarrow$$BF_3$ we have localized the corresponding minima (the number of corresponding values for the Hess matrix $\lambda = 0$) of the complexes **1-5**. As a result, the thermodynamically stable isomers **1a**,**b**, and **4a**,**b** were found with a different position of the acceptor fragment relative to the double bond of the 5-diazouracil C=O bond.

The most significant calculated data are given in Table 1 with labelling of the interatomic distances as shown on structure **1a** in Scheme 1. According to this data the total energies (E) of the 5-diazouracil and boron trifluoride are -517.17714 and -321.46584 a.u. respectively and, hence, the most stable prove to be the systems **1b**, **3**, and **4a** (the stabilization energies E_{st} of the complexes are given in Table 1).

In the series of complexes studied the system **2** stands out in which the N···B distance between the coordination centers is large, the geometry of the BF_3 acceptor part is planar, and the stabilization energy is minimal. In all the remaining examples a marked shortening of the X···B distance along with a pyramidal BF_3 fragment.

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* For Communication 1 see [1].

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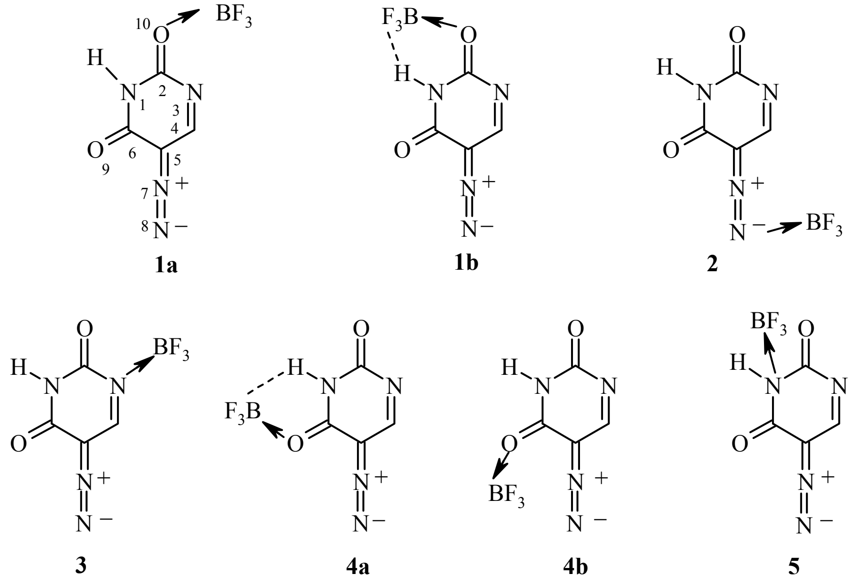
Scheme 1



The structure of the systems **1b** and **4a** is also curious in that it is stabilized by intramolecular attractive interactions as N–H···F–B four centered fragments. Moreover, in both **1b** and **4a** systems, there is a sharp increase in the B···F distance (to 1.408 and 1.402 Å respectively) and also a shortening of the H···F distance (1.730 and 1.785 Å respectively).

TABLE 1. Calculated Geometries and Energy Parameters for Complexes **1-5***

Complex	Parameter						
	l_{102}	l_{23}	l_{34}	l_{45}	l_{57}	l_{78}	l_{56}
1a, C_s	1.239	1.371	1.285	1.412	1.330	1.095	1.447
1b, C_s	1.249	1.371	1.286	1.409	1.330	1.095	1.449
2, C_s	1.200	1.411	1.269	1.433	1.306	1.104	1.454
3, C_s	1.195	1.414	1.292	1.391	1.335	1.093	1.454
4a, C_s	1.195	1.405	1.270	1.430	1.327	1.095	1.416
4b, C_s	1.196	1.398	1.270	1.435	1.337	1.090	1.420
5, C_1	1.188	1.387	1.272	1.429	1.320	1.099	1.437

Complex	Parameter					
	l_{69}	l_{18}	l_{12}	l_{XB}	*E*, a.u.	E_{st}, kcal/mol
1a, C_s	1.210	1.388	1.359	1.634	-838.68804	28.3
1b, C_s	1.209	1.386	1.352	1.593	-838.70087	36.3
2, C_s	1.214	1.370	1.400	2.722	-838.64695	2.5
3, C_s	1.211	1.372	1.391	1.662	-838.70555	39.3
4a, C_s	1.265	1.327	1.420	1.594	-838.70133	36.6
4b, C_s	1.256	1.343	1.416	1.596	-838.69320	31.5
5, C_1	1.200	1.446	1.482	1.841	-838.65265	6.0

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* l_{ij} = bond length; X = coordination center.

In order to estimate the "additional" stabilization in **1b** and **4a** (i.e. the attractive interaction) one can use the difference in their energy from the energy of the less stable isomeric forms **1a** and **4b** which are 8.1 and 5.8 kcal/mol respectively.

Hence, according to calculated data, the most likely centers for the coordination of the boron trifluoride in the catalytic processes are the positions 3, 9, and 10 of the 5-diazouracil molecule.

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