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A DFT STUDY OF CONFORMATIONS AND ELECTRONIC STRUCTURE OF N-METHYLUREAA. A. Sorvanov

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E-mail: wellitson@gmail.com**ИССЛЕДОВАНИЕ КОНФОРМАЦИИ И ЭЛЕКТРОННОЙ СТРУКТУРЫ N-МЕТИЛМОЧЕВИНЫ
МЕТОДОМ ФУНКЦИОНАЛА ПЛОТНОСТИ**А.А. Сорванов

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Аннотация. В настоящей работе методами DFT и HF с использованием пакета программ для квантово-химических расчетов Gaussian проведен конформационный анализ N-метилмочевины в растворе ДМСО. Окружение молекулы учитывалось в рамках модели непрерывной поляризуемой среды РСМ. Выполнено исследование стереоэлектронных взаимодействий методом NBO, произведен расчет энергий граничных орбиталей.

Introduction. Urea related systems is an important class of organic compounds that finds various application in fundamental and applied science. Large number of urea derivatives find application as agrochemicals, dyes for cellulose fibers, gasoline antioxidants, etc. Urea derivatives also have displayed a wide spectrum of biological activity. Moreover, urea and its alkyl-substituted derivatives exhibit second-harmonic generation nonlinearity, which makes it a subject of a great interest for physicist. Knowledge of the shapes and energetics of urea molecules is essential for understanding rich chemistry of this functional group. Quantum chemical methods are important to obtain information about molecular structure and electrochemical behavior. However, electronic structure calculations dedicated to urea derivatives are few in number.

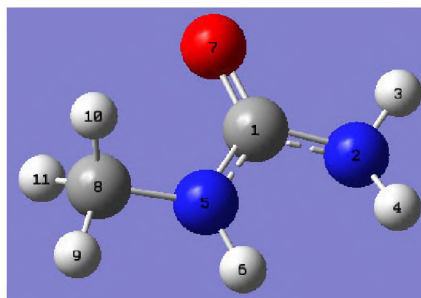


Fig.1. N- methylurea molecular structure

Materials and methods. In this work, we have report conformational analysis for N-methylurea performed with density-functional theory (DFT), Hartree-Fock (HF) and second order Moller-Plesser perturbation theory. All minima and maxima obtained from rotation around N-C bond have been considered and

fully optimized. The Natural Bond Orbitals (NBO) analysis also have been performed for these structures in order to understand differences in stability of N-monomethylurea conformers by observing various second-order interactions between the filled orbitals and vacant orbitals.

Results and discussion. Prior studies have identified two nonplanar minima of N-methylurea – cis and trans – that are interconverted by rotation around C_a-N. Figure 2 illustrates the potential electronic surface (PES) for the rotation of the methyl group in N-methylurea at three different level of theory: B3LYP/6-311++G(2d,p), MP2-FC/6-311+G(d,p) and HF/6-311++G(2d,p). Each curve has approximately the same shape with a little difference in energy values. However, MP2 and HF methods are exhibit a small energy barrier around 180 degrees, while scrupulous DFT analysis shows no evidence of transition states in this area.

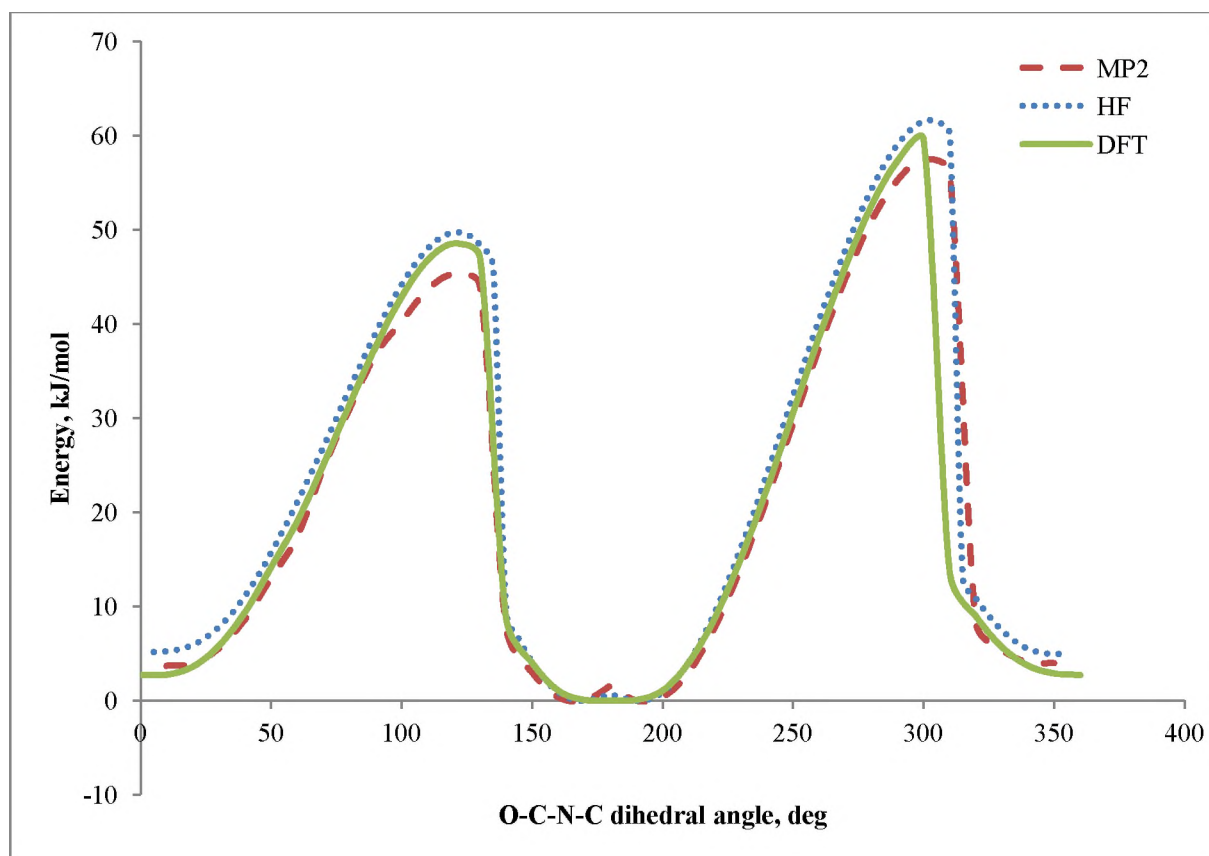


Fig. 2. PES for N-C bond rotation in N-methylurea at various level of theory

Relative energies and optimized geometric parameters of conformers are summarized in Table 1. The energy of the two important frontier molecular orbitals such as the highest occupied molecular orbitals (HOMO), the lowest unoccupied molecular orbitals (LUMO) have been calculated using B3LYP/6-311++G(d,p) level. The energy gap of HOMO-LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. The values of energy of the LUMO and the HOMO and HOMO-LUMO energy gap (E_g) of conformers 1-6 are also presented in Table 1. NBO analysis is a common method for investigation of stereoelectronic effects and gives information about energy of the interactions between filled Lewis type NBOs and empty non-Lewis type NBOs. These intra-molecular interactions between orbitals can strengthen and weaken bonds in the molecular system. In this study NBO calculations were performed by the UB3LYP level of theory with 6-311++G(2d,p) basis in order to investigate the intramolecular

bonding interactions influence on stability of certain N-methylurea conformers. The second order perturbation energy values $E(2)$ are collected in Table 2.

Table 1

Geometric parameters and calculated energies of conformers 1-6

Feature	I	TS1	II	TS2	Experiment [1]
Bond Length					
C=O	1.234	1.222	1.238	1.225	1.233 ± 0.011
C1-N2	1.381	1.351	1.374	1.345	1.373 ± 0.036
C1-N5	1.362	1.441	1.360	1.445	1.337 ± 0.011
N5-C8	1.454	1.474	1.455	1.478	1.442 ± 0.014
Bond Angles					
N2-C1-O7	121.7	122.5	121.6	123.6	121.2 ± 2.0
N2-C1-N5	115.6	116.4	116.5	112.4	116.0 ± 1.5
C1-N5-C8	121.3	115.2	126.1	112	121.7 ± 1.0
Dihedral Angles					
O-C1-N5-C8	0	121	187	300	0 ± 2.4 (0-8.6)
O-C1-N5-H6	-158.8	-115.0	-5.3	57.9	180 ± 5.8 (155-180)
E_{total} , kJ/mol	0	59.05	2.22	48.05	
$E(\text{LUMO})$, eV	-0.28	-0.37	-0.28	-0.34	
$E(\text{HOMO})$, eV	-7.15	-7.07	-7.15	-6.71	
$E \Delta E$, eV	6.87	6.7	6.87	6.37	

Interactions $\text{LP O7} \rightarrow \text{BD}^* (\text{C1-N2})$, $\text{LP O7} \rightarrow \text{BD}^* (\text{C1-N5})$ are common for all urea-based molecules and have close values for all observed conformers.

Table 2

Significant donor-acceptor interactions and second order perturbation energies of 1-4

Donor	Acceptor	$E(2)$, kcal/mol			
		I	TS1	II	TS2
BD C1-N5	$\text{BD}^*(2) \text{ C1 - N5}$	28.03	-	-	-
BD C1-N5	$\text{BD}^*(1) \text{ C1 - O7}$	43.86	-	-	-
BD C1-N5	$\text{BD}^*(2) \text{ C1 - O7}$	36.24	-	-	-
BD C1-O7	$\text{BD}^*(2) \text{ C1 - N5}$	90.10	-	-	-
BD C1-O7	$\text{BD}^*(1) \text{ C1 - O7}$	18.69	-	-	-
BD C1-O7	$\text{BD}^*(2) \text{ C1 - O7}$	70.16	-	-	-
BD C1-O7	$\text{BD}^*(2) \text{ C1 - N5}$	81.77	-	-	-
BD C1-O7	$\text{BD}^*(1) \text{ C1 - O7}$	75.73	-	-	-
BD C1-O7	$\text{BD}^*(2) \text{ C1 - O7}$	13.23	-	-	-
BD C1-O7	$\text{LP}^*(1) \text{ C1}$	-	-	38.75	-
LP N2	$\text{BD}^*(2) \text{ C1 - O7}$	-	35.82	-	29.67
LP N5	$\text{LP}^*(1) \text{ C1}$	-	-	61.24	-
LP O7	$\text{BD}^*(1) \text{ C1 - N2}$	11.38	11.51	11.33	11.49
LP O7	$\text{BD}^*(1) \text{ C1 - N5}$	11.04	12.24	10.61	12.51
LP O7	$\text{LP}^*(1) \text{ C1}$	-	-	111.26	-
$\text{BD}^*(2) \text{ C1 - N5}$	$\text{RY}^*(1) \text{ C1}$	12.88	-	-	-
$\text{BD}^*(1) \text{ C1 - O7}$	$\text{BD}^*(2) \text{ C1 - N5}$	394.16	-	-	-
$\text{BD}^*(2) \text{ C1 - O7}$	$\text{BD}^*(2) \text{ C1 - N5}$	271.09	-	-	-
$\text{BD}^*(2) \text{ C1 - O7}$	$\text{BD}^*(1) \text{ C1 - O7}$	389.64	-	-	-

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