



дхн Васил Борисов Делчев

**Списък с публикации, наукометрия и
резюмета на материалите (по чл. 76 (1) от
ПРАСПУ) и самооценка на приносите**

по конкурс за “ПРОФЕСОР” по Физикохимия

4. Природни науки, математика и информатика,

4.2. Химически науки



СПИСЪК НА ПУБЛИКАЦИИТЕ

№	НАУЧНИ ПУБЛИКАЦИИ	Участие в процедури
1998		
1	P. Y. Malakov, G. Y. Papanov, V. Deltchev , "11-Episcutecolumnin C, A neo-clerodane diterpenoid from <i>Scutellaria Columnae</i> " (1998) <i>Phytochemistry</i> , 49:3 , 811-815.	доцент
2	Г. Ст. Николов, В. Делчев , "Квантовохимично изследване на кето-енолното равновесие при малонов алдехид" (1998) <i>Съюз на учените в България - Пловдив, Юбилейна научна сесия, Сборник на докладите и резюметата</i> , Пловдив, III , 217-220.	доцент
2000		
3	V. Delchev , G. St. Nikolov, "Ab initio study of the keto-enol equilibrium of malonaldehyde" (2000) <i>Monatshefte für Chemie</i> , 131:2 , 99-105.	доктор доцент професор
4	V. Delchev , G. St. Nikolov, "Ab initio study of malonaldehyde rotamers" (2000) <i>Monatshefte für Chemie</i> , 131:2 , 107-115.	доктор доцент
5	В. Делчев , "Квантовохимично изучаване на кето-енолната тавтомерия на ацетилацетона с метода на Hartree-Fock и базисни функции STO-3G**" (2000) <i>Пловдивски университет, Научни трудове</i> , 29:5 , 79-85.	доцент
2001		
6	V. Delchev , H. Mikosch, "An ab initio study of the rotamers and rotations of propane-1,3-dial by DFT and SCF calculations" (2001) <i>Monatshefte für Chemie</i> , 132:2 , 223-233.	доктор доцент ДХН
7	V. Delchev , H. Mikosch, G. St. Nikolov, "The keto-enol equilibrium of pentane-2,4-dione studied by ab initio methods" (2001) <i>Monatshefte für Chemie</i> , 132:3 , 339-348.	доктор доцент професор
8	P. Y. Malakov, G. Y. Papanov, V. Deltchev , "Chemical transformations of montanin B" (2001) <i>Annual of Sofia University</i> , 91 , 125-131.	доцент
2002		
9	N. Trendafilova, G. Bauer, I. Georgieva, V. Delchev , "Conformational stability and vibrational spectrum of glyoxilic acid oxime predicted from <i>ab initio</i> study" (2002) <i>Journal of Molecular Structure</i> , 604 , 211-220.	доцент
10	П. Я. Малаков, Г. Я. Папанов, В. Делчев , "Нео-клеродани изолирани от видовете на род <i>Ajuga</i> и <i>Scutellaria</i> , разпространени в България" (2002) <i>Научни трудове, Пловдивски университет</i> , 31:5 , 41-59.	доцент
11	Д. Христозова, В. Делчев , Г. Н. Андреев, "Електронен строеж и структура на тавтомерните форми на 2-(2',4'-динитробензил)пиридин" (2002) <i>Научни трудове, Пловдивски университет</i> , 31:5 , 115-120.	доцент
2003		
12	G. N. Andreev, B. Schrader, D. A. Hristozova, V. B. Delchev , J. S. Petrov, P. Rademacher, "Vibrational spectra and structure of the photochromic 2-(2',4'-dinitrobenzyl) pyridine" (2003) <i>Journal of Molecular Structure</i> , 645:1 , 77-87.	доцент
13	V. B. Delchev , "Conformational analysis of planar enol rotamers of 2,4-pentanedione: an ab initio study" (2003) <i>Journal of Structural Chemistry</i> , 44:4 , 630-636.	доцент ДХН



2004

14	V. B. Delchev, "DFT ab initio study of the keto-enol tautomerism of barbituric acid" (2004) <i>Journal of Structural Chemistry</i> , 45:4 , 602-610.	доцент ДХН професор
15	V. B. Delchev, "Hydrogen bonded complexes of acetylacetone and methanol: HF and DFT level study" (2004) <i>Monatshefte für Chemie</i> , 135:3 , 249-260.	доцент ДХН
16	V. B. Delchev, "A DFT study of electron structure, geometry, and keto-enol tautomerism of 3-oxopropionyl halogenides" (2004) <i>Monatshefte für Chemie</i> , 135:4 , 371-384.	доцент ДХН професор
17	В. Б. Делчев, "Фазовые равновесия в системах ацетилацетон-вода-спирт (метанол, этанол, изопропанол)" (2004) <i>Журнал Физической Химии</i> , 78:1 , 34-37.	професор
18	В. Б. Делчев, Х. Микош, "Ab initio изучаване на кето-енолната тавтомерия на гуанин в газова фаза" (2004) <i>Научни трудове на Съюза на учените в Пловдив</i> , IV , 130-135.	доцент ДХН
19	V. B. Delchev, H. Mikosch, "Theoretical study of 2,4-pentanedione enol form conformers and their interconversions at DFT and HF levels" (2004) <i>Russian Journal of Physical Chemistry</i> , 78:9 , 1445-1452.	доцент ДХН професор
20	V. B. Delchev, H. Mikosch, "Electron and geometry structure of hydrogen-bonded complexes of guanine with one molecule methanol. A DFT level study" (2004) <i>Monatshefte für Chemie</i> , 135:11 , 1373-1387.	доцент ДХН

2005

21	V. Delchev, H. Mikosch, "Gas phase ionization of 1,3-propanedial tautomeric forms: a theoretical study" (2005) <i>Journal of Structural Chemistry</i> , 46:3 , 422-429.	доцент
22	В. Б. Делчев, Х. Микош, "Сравнително разглеждане на амин-иминната тавтомерия в аденин с метода на Хартри-Фок и теорията за функционала на плътността" (2005) <i>Научни трудове, Пловдивски университет</i> , 32:5 , 95-100.	доцент професор
23	В. Б. Делчев, Х. Микош, "Изучаване на кето-енолната тавтомерия в малонилцистеамина с помощта на теорията за функционала на плътността" (2005) <i>Съюз на учените в България – Пловдив, серия Б. Естествени и хуманитарни науки</i> , V , 7-12.	доцент ДХН професор
24	И. Иванов, Ст. Статкова-Абегхе, П. Ангелов и В. Делчев, "Региоселективност при циклизация по Pictet – Spengler на N-[2-(2-ацил-4,5-диметокси-фенил)етил]-амиди" (2005) <i>Съюз на учените в България – Пловдив, серия Б. Естествени и хуманитарни науки</i> , V , 35-37.	
25	V. B. Delchev, H. Mikosch, "H-bonded complexes between acetylacetone and two molecules of methanol: HF and DFT level study" (2005) <i>Journal of Molecular Modeling</i> , 11:6 , 474-480.	доцент ДХН
26	V. B. Delchev, H. Mikosch, "Investigation of the intermolecular proton transfer in the supersystem adenine-methanol: a DFT level study" (2005) <i>Scientific researches of the Union of Scientists in Bulgaria – Plovdiv, Series C. Technics and Technologies, Balkan Conference of Young Scientists</i> , 16-18 June 2005, 5 , 303-308.	доцент професор
27	R. I. Bakalska, V. B. Delchev, D. S. Vassilev, G. T. Delcheva, "Stereoselective synthesis of 2-pyridono-2-pyrrolidono- and azolo[1,5-a] pyrimidinomorphinans by means of cascade reaction of codeinone and amides of α -methylene active acids and 5-aminotetrazole" (2005) <i>Scientific researches of the Union of Scientists in Bulgaria – Plovdiv, Series C. Technics and Technologies, Balkan Conference of Young Scientists</i> , 16-18 June 2005, 5 , 296-302.	доцент
28	V. Delchev, D. Hristozova, A. Terziyski, J. Petrov, "Thermodynamic analysis of the stable isomers of Adamantylidene-[1-(2,5-dimethyl-3-furyl)ethylidene]succinic	доцент



	anhydride: a DFT level study" (2005) <i>Bulgarian Chemical Communications</i> , 37:4 , 344-349.	
2006		
29	V. B. Delchev, H. Mikosch, "DFT study of the gas phase proton transfer in guanine assisted by water, methanol and hydrogen peroxide" (2006) <i>Journal of Molecular Modeling</i> , 12:2 , 229-236.	доцент ДХН професор
30	V. B. Delchev, H. Mikosch, "Theoretical study of the hydrogen-bonded complexes serotonin-water/hydrogen peroxide" (2006) <i>Journal of Molecular Modeling</i> , 12:3 , 272-280.	доцент ДХН
31	V. B. Delchev, H. Mikosch, "Selection of a quantum-chemical method and basis set for optimization of the complex ion $\text{Cu}(\text{H}_2\text{O})^{+}$ " (2006) <i>Journal of Structural Chemistry</i> , 47:5 , 985-989.	доцент
32	И. Г. Щерев, В. Б. Делчев, "Теоретично изследване на изомерните превръщания на урацил в газова фаза" (2006) <i>Научни трудове на ПУ</i> , 34:5 , 105-111.	ДХН професор
2007		
33	V. B. Delchev, H. Mikosch, "Theoretical study of the intermolecular H-bonding and intermolecular proton transfer between isocytosine tautomeric forms and R,S-lactic acid" (2007) <i>Journal of Molecular Modeling</i> , 13:1 , 19-28	доцент професор
34	I. G. Shterev, V. B. Delchev, "Conformational landscape of the enol form conformers of thiomalonaldehyde: DFT and MP2 level study" (2007) <i>Bulgarian Chemical Communications</i> , 39:2 , 88-97.	ДХН
35	V. B. Delchev, I. G. Shterev, "Theoretical study of the tautomeric forms of acetylacetone: HF and DFT level of investigation" (2007) <i>Bulgarian Chemical Communications</i> , 39:2 , 98-105.	професор
36	V. B. Delchev, G. T. Delcheva, "DFT Study of the Oxaloacetic acid Condensation – the First Step of the Citric Acid Cycle" (2007) <i>Journal of Structural Chemistry</i> , 48:4 , 666-673.	професор
37	V. B. Delchev, I. G. Shterev, H. Mikosch, N. T. Kochev, "Investigation of the intermolecular proton transfer in the supersystems adenine – methanol/ethanol/i-propanol: MP2 and DFT levels study" (2007) <i>Journal of Molecular Modeling</i> , 13:9 , 1001-1008.	професор
2008		
38	V. B. Delchev, "Experimental and theoretical study of the heterogeneous equilibrium in the ternary system water + ethanol + <i>i</i> -pentanol" (2007) <i>Scientific researches of the Union of Scientists – Plovdiv, Series C, Technics and Technologies (International conference of young scientists)</i> , VI , 165-170.	
39	V. B. Delchev, M. Nenkova, "Theoretical modeling of the ground state intramolecular proton transfer in cytosine: DFT level study" (2008) <i>Acta Chimica Slovenica</i> , 55 , 132-137.	ДХН професор
40	V. B. Delchev, I. G. Shterev, H. Mikosch, "Theoretical investigation (DFT and MP2) of the intermolecular proton transfer in the supersystems uracil-(H_2O) _n and uracil-(CH_3OH) _n (n=1,2)" (2008) <i>Monatshefte für Chemie</i> , 139 , 349-362.	ДХН професор
2009		
41	V. B. Delchev, I. G. Shterev, "Ground state intermolecular proton transfer in the supersystems thymine-(H_2O) _n and thymine-(CH_3OH) _n , n=1,2: a theoretical study" <i>Journal of Molecular Modeling</i> (2009) 15:4 , 411-419	ДХН професор
42	I. G. Shterev, V. B. Delchev, "Theoretical investigation of the intermolecular H-bonding and proton transfer in cytosine assisted by water and methanol" (2009) <i>Monatshefte für Chemie</i> , 140:11 , 1381-1394.	ДХН професор
43	S. Georgiev, R. Karaminkov, S. Chervenkov, V. Delchev, H. J. Neusser, "Mass-Analyzed Threshold Ionization Spectroscopy of 2-Phenylethanol: Probing	професор



	of Conformational Changes Caused by Ionization" (2009) <i>Journal of Physical Chemistry A</i> , 113:44 , 12328-12336.	
2010		
44	V. B. Delchev, "Semi-diabatic PESs of the photo-induced rotations of the stable enol form of acetylacetone around the C=C and C-O bonds: TD B3LYP level study" (2010) <i>Asian Chemistry Letters</i> , 14:3 , 267-272.	професор
45	V. B. Delchev, "Computational (DFT and TD DFT) study of the electron structure of the tautomers / conformers of uridine and deoxyuridine and the processes of intramolecular proton transfers" (2010) <i>J. Mol. Mod.</i> , 16:4 , 749-757.	ДХН професор
46	V. B. Delchev, W. Domcke, "Cyclodimerization of DNA and RNA bases: <i>Ab initio</i> study of the cyclodimerization of the uracil dimer through a butane-like conical intersection" (2010) <i>High Performance Computing in Science and Engineering, Garching/Munich 2009, Part 7</i> , 709-718, DOI: 10.1007/978-3-642-13872-0_59 (Springer)	ДХН професор
47	V. B. Delchev, Andrzej L. Sobolewski, Wolfgang Domcke, "Comparison of the non-radiative decay mechanisms of 4-pyrimidinone and uracil: an <i>ab initio</i> study" (2010) <i>Phys. Chem. Chem. Phys.</i> , 12 , 5007 – 5015.	ДХН професор
48	V. B. Delchev, "Photoinduced conformational transformation of the hydroxy form of uridine and deoxyuridine and hydrogen detachment in oxo and hydroxy tautomers of the compounds: a computational study" (2010) <i>Monatshefte für Chemie</i> , 141:10 , 1153 –1157.	ДХН професор
49	V. B. Delchev, "Face-to-back" photo-cyclodimerization of the malonaldehyde enol form with the strong intramolecular H-bond: A TD DFT theoretical study" (2010) <i>J. Mol. Struct. THEOCHEM</i> , 958 , 101-105.	ДХН професор
2011		
50	V. B. Delchev, "The shape of the conical intersections of monohydrated pyrimidine bases cytosine, uracil, and thymine: a theoretical study" (2011) <i>Monatshefte für Chemie</i> , 142:3 , 251-260.	професор
51	V. B. Delchev, Ivan G. Shterev, "Local characterization of the conical intersection of the cyclodimerization reaction of the malonaldehyde enol form: an <i>ab initio</i> study" (2011) <i>Asian Chemistry Letters</i> , 15:1,2 , 59-66.	ДХН професор
52	V. B. Delchev, Ivan G. Shterev, "Photoinduced disruption of the strong intramolecular H-bond in the enol form of acetylacetone: mechanisms of radiationless decay" (2011) <i>Computational and Theoretical Chemistry</i> , 967 , 152-159.	ДХН професор
53	R. Karaminkov, S. Chervenkov, V. Delchev, H. Neusser, "High-Resolution Mass-Selective UV Spectroscopy of Pseudoephedrine: Evidence for Conformer-Specific Fragmentation" (2011) <i>J. Phys. Chem. A</i> , 115:34 , 9704–9713.	професор
54	В. Б. Делчев, И. П. Иванова, "Изследване на реакционните пътища на възбудените състояния при NH- и CH- дисоциация на барбитуровата киселина" (2011) <i>Сборник доклади, Юбилейна национална научна конференция с международно участие "Човекът и Вселената", СУБ-Смолян, първо издание, 6-8 Октомври 2011, 379-383. (ISBN: 978-954-397-025-4)</i>	ДХН професор
55	P. B. Kancheva, V.B. Delchev, "Excited-state reaction paths of cytosine and isocytosine: C=O elongation" (2011) <i>Научни трудове ПУ</i> , 38:5 , 71-80.	професор
2012		
56	R. Bakalska, V. B. Delchev, "Photoinduced tautomerism of 2-thiobarbituric acid studied by theoretical and experimental methods" (2012) <i>Acta Chim. Slov.</i> , 59 , 75-82.	ДХН професор
57	I. G. Shterev, V. B. Delchev, "Excited-state deactivation of the monohydrated complexes of cytosine, uracil and thymine through S ₀ /S ₁ conical intersections"	ДХН професор



	(2012) <i>Monatshefte für Chemie</i> , 143 , 763-770.	
58	V. B. Delchev, I. P. Ivanova, "Theoretical study of the excited-state reaction paths of the OH- and NH-dissociation processes in barbituric acid" (2012) <i>Monatshefte für Chemie</i> , 143 , 1141-1150	професор
59	R. I. Bakalska, V. B. Delchev, "Comparative study of the relaxation mechanisms of the excited states of cytosine and isocytosine" (2012) <i>J. Mol. Mod.</i> , 18 , 5133-5146.	професор
60	И. Г. Щерев, И. И. Тошев, В. Б. Делчев, "Теоретично изучаване на водородно свързаните комплекси на серотонина с n молекули вода (n=1, 2, 3, 4, 5, 6 и 7)" (2012) <i>Научни трудове на УХТ</i> , LIX , 389-394.	професор
61	И. Г. Щерев, Н. Т. Николов, В. Б. Делчев, "Ефекти на хидратираната вода върху вертикалните енергии на възбуждане на водородно свързаните комплекси на серотонина с вода" (2012) <i>Научни трудове на УХТ</i> , LIX , 636-640.	професор
2013		
62	V. B. Delchev, "Excited-state relaxation paths of oxo / hydroxy and N9H / N7H tautomers of guanine: a CC2 theoretical study" (2013) <i>J. Mol. Mod.</i> , 19 , 2299-2308.	професор
63	В. Б. Делчев, "Конични сечения S ₀ /S ₁ при гуанина, свързани с деформация на пуриновия пръстен" (2013) <i>Сборник доклади на Юбилейната национална научна конференция с международно участие "Традиции, посоки, предизвикателства", Смолян 19-21 октомври 2012</i> , III , 203-207.	професор
64	V. B. Delchev, "Comparative study of the O...H...O proton transfer in the enol form of a single acetylacetone molecule and acetylacetone incorporated in β-cyclodextrin: a theoretical investigation" (2013) <i>Monatshefte für Chemie</i> , 144 , 1153-1158.	професор
65	V. B. Delchev, W. Domcke, "Ab initio study of the cyclodimerization of uracil through butane-like and oxetane-like conical intersections" (2013) <i>J. Photochem. Photobiol. A: Chemistry</i> , 271 , 1-7.	професор
66	И. Щерев, М. Говедаров, В. Делчев, "Сравнително разглеждане на вътрешномолекулния и (ин)директния межумолекулен протонен пренос в тимина: DFT изследване" (2013) <i>Научни трудове (УХТ)</i> , LX , 734-738.	професор
67	И. Щерев, Д. Димитрова, В. Делчев, "Сравнително DFT изследване на механизма на N-H фотодисоциация в оксо формата на барбитуровата киселина в газова фаза и разтворител етанол" (2013) <i>Научни трудове (УХТ)</i> , LX , 679-683.	професор
2014		
68	I. G. Shterev, V. B. Delchev, "Solvent influence on the excited states of the oxo form of barbituric acid and the mechanisms of the out-of-plane non-radiative elongation of the out-of-plane nonradiative elongation of the N-H bond: a comparative theoretical and experimental study" (2014) <i>Spectrochimica Acta Part A</i> , 125 , 384-390.	професор
69	C. Rabong, C. Schuster, T. Liptaj, N. Prónayová, V. B. Delchev, U. Jordis, J. Phopase, "NXO beta structure mimicry: an ultrashort turn/hairpin mimic that folds in water" (2014) <i>RSC Advances</i> , 4 , 21351-21360.	професор
70	V. B. Delchev, "Xanthine and hypoxanthine: in a search for conical intersections S ₀ /S ₁ connected with deformations of pyrimidine residue of the purine ring" (2014) <i>Bulg. Chem. Commun. (Special Issue)</i> , 46 , 203-208.	професор
71	V. B. Delchev, K. B. Gavazov, I. G. Shterev, "Ground- and excited-state stability of the conformers of 3,5-dinitrocatechol and its complexes with W(VI) and V(V): combined theoretical and experimental study" (2014) <i>J. Mol. Mod.</i> 20 , 2549(8)	професор



2015

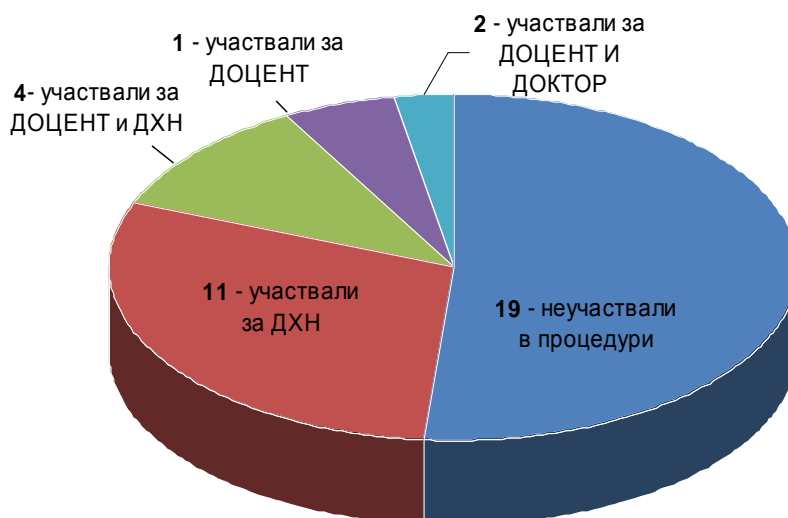
72	P. Marinova, M. Marinov, V. Delchev, N. Stoyanov, "New platinum(II) complexes of cycloalkanespiro-5-(2-thiohydantoin)s. Synthesis and quantum chemical investigation" (2015) <i>Acta Chimica Slovenica</i> , 62 , 225-232	
73	K. B. Gavazov, V. B. Delchev, G. K. Toncheva, Z. G. Georgieva, "Extraction-Spectrophotometric and Theoretical (Hartree-Fock) Investigations on a Ternary Complex of Iron(II) with 4-Nitrocatechol and 2,3,5-Triphenyl-2H-tetrazolium" (2015) <i>Russ. J. General Chem.</i> , 85:8 , 1945-1951	професор
74	I. G. Shterev, V. B. Delchev, "Excited-state deactivation channels via internal conversions in two position isomers of hydroxy-methyl-pyridine: a theoretical study" (2015) <i>J. Phys. Org. Chem.</i> , 28 , 681-689.	професор

2016

75	K. B. Gavazov, V. B. Delchev, T. S. Stefanova, G. K. Toncheva, and K. K. Simitchiev, "Specific Features of Tetranitrotetrazolium Blue Chloride as an Extraction Reagent for Iron(III)" (2016) <i>Russ. J. General Chem.</i> - accepted	професор
76	P. Kancheva, D. Tuna, V. B. Delchev, "Comparative study of radiationless deactivation mechanisms in cytosine and 2,4-diaminopyrimidine" (2016) <i>J. Photochem. Photobiol. A</i> , 321 , 266-274.	професор

РАЗБОР НА ПУБЛИКАЦИИТЕ ПО КОНКУРСА ЗА "ПРОФЕСОР"

- статии с ИФ (в чужди, специализирани списания, появили се във вторични литературни източници)



- статии без ИФ



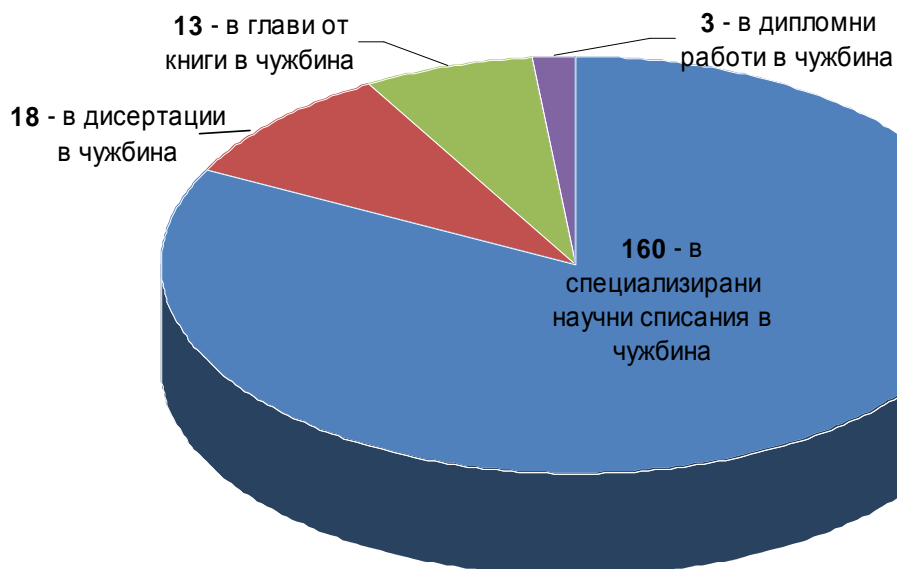


РАЗБОР НА ЦИТИРАНИЯТА ПО КОНКУРСА ЗА “ПРОФЕСОР”

- участвали в процедури



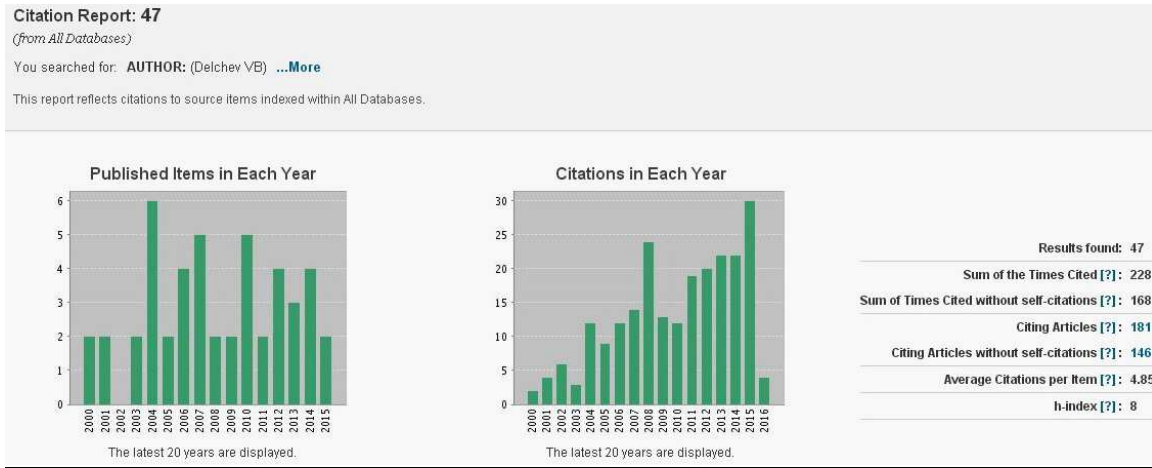
- в зависимост от източника



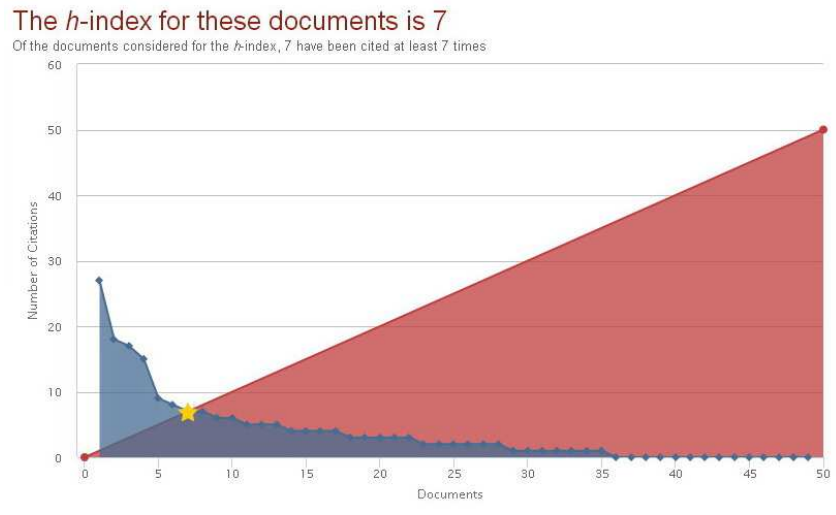


ИНФОРМАЦИЯ ОТ ISI WEB-OF-SCIENCE, SCOPUS И GOOGLE SCHOLAR

ISI



SCOPUS



Google scholar





РЕЗЮМЕТА НА НАУЧНИТЕ ПУБЛИКАЦИИ

- 3 V. Delchev, G. St. Nikolov, "Ab initio study of the keto-enol equilibrium of malonaldehyde" (2000) *Monatshefte für Chemie*, **131:2**, 99-105. **IF = 0.783**

Abstract. The mechanism of the keto-enol tautomerism of malonaldehyde was studied by ab initio methods using 6-21G** and 6-311G** basis functions at the HF level. Two separate mechanisms were examined: through-space proton transfer in the ω -shaped form and through-space proton transfer in a sickle-shaped form obtained from the ω form by rotation. The transition state structure of the ω form is non-planar, whereas that of the sickle form is planar. The sickle form is connected with a 2nd order saddle, indicating that there should exist a lower energy barrier, i.e. that the throughbond mechanism may be preferred. The calculated energy barriers of keto-enol tautomerism for the sickle form is twice as high as those for the omega form.

- 7 V. Delchev, H. Mikosch, G. St. Nikolov, "The keto-enol equilibrium of pentane-2,4-dione studied by ab initio methods" (2001) *Monatshefte für Chemie*, **132:3**, 339-348. **IF = 0.821**

Abstract. The mechanism of the keto-enol interconversion of pentane-2,4-dione (trivial name: acetylacetone, acac) was examined at the restricted Hartree-Fock (HF) level and the DFT correlation functional BLYP method using the 6-311G** basis, both included in the program GAUSSIAN 98. Two initial enol forms are considered: the omega and sickle forms, related by a rotation of 180° around the OC-CC bond. The study is restricted to the through-space transfer of the hydroxyl proton to C(2). The two geometry-optimized enol forms are planar; the geometry optimization of the diketone forms leads to the same non-planar structure, regardless of the starting enol geometry. The transition state of the through-space omega-enol→diketone conversion has also a non-planar structure, indicating that the hydroxyl proton moves outside of the CCC plane. The BLYP-calculated energy barrier of the forward (omega-enol→diketone) conversion is 245 kJ mol⁻¹, that of the reverse (diketone→omega-enol) conversion 222 kJ mol⁻¹; thus, an almost symmetric barrier, which is not thermally accessible, is defined. The energy barrier for the sickle-enol→diketone conversion is considerably lower (187 kJ mol⁻¹), to access the sickle form from the more stable omega form, a rotation is needed (energy barrier: 88 kJ mol⁻¹). The HF-calculated barriers are 1.3-1.4 times higher than those obtained with the BLYP method.

- 14 V. B. Delchev, "DFT ab initio study of the keto-enol tautomerism of barbituric acid" (2004) *Journal of Structural Chemistry*, **45:4**, 602-610. **IF = 0.472**

Abstract. Eight possible tautomeric forms of barbituric acid have been studied using the Gaussian-98 program at a B3LYP/D95** level of computation. All of them are considered in the isolated state in order to find the transition states between pairs of tautomers. The energies of the transition states were used for subsequent estimation of the energy barriers of the tautomeric transformations.

- 16 V. B. Delchev, "A DFT study of electron structure, geometry, and keto-enol tautomerism of 3-oxopropionyl halogenides" (2004) *Monatshefte für Chemie*, **135:4**, 371-384. **IF = 0.904**

Abstract. The electronic and geometry structures of all enol and diketofoms of 3-oxopropionyl halogenides were investigated at the B3LYP/3-21G** level of theory. The comparative study of their energies revealed that the enol forms of the compounds are more stable than *cis*- and *trans*-diketones. All *cis*-diketones (except Cl-containing one) have one imaginary frequency in their vibration spectra, i.e. they do not correspond to local or global minima on the potential hypersurface. The keto-enol transformations enol↔*cis*-diketone and enol↔*trans*-diketone for a certain triad of tautomers / isomers pass through one



transition state or in other words, the two conversions have one common maximum on the energy hypersurface. The energy barriers of the keto–enol conversions found for isolated molecules are quite high. Only for the enol→diketone conversions in solution the energy barriers are slightly reduced.

- 17 V. B. Delchev**, “Phase Equilibria in the Three-Component Systems Acetylacetone–Water–Methanol/Ethanol/*i*-Propanol at Room Temperature) (2004) **IF = 0.414**
Russian Journal of Physical Chemistry, **78:1**, 29-32.

Abstract. Three liquid systems have been studied in order to build and estimate the phase curves separating their homogeneous and heterogeneous areas defined by the mutual solubility of three liquid components: acetylacetone, water, and one of alcohols—MeOH/EtOH/*i*-PrOH. The results showed that the heterogeneous area is larger in the methanol-containing system. We explain this experimental fact, keeping in mind that the methanol can form stronger intermolecular H-bonds with other molecules in the solution than the other two alcohols. We also found correlations between the volume concentrations of the components in the critical (phase) points that have high correlation coefficients.

- 19 V. B. Delchev**, H. Mikosch, “Theoretical study of 2,4-pentanedione enol form conformers and their interconversions at DFT and HF levels” (2004) *Russian Journal of Physical Chemistry*, **78:9**, 1445-1452. **IF = 0.414**

Abstract. The conformational stability of eight planar conformers of the enol form of 2,4-pentanedione and their interconversions were studied at the HF and DFT levels of theory. The conformers were optimized in their singlet ground states by means of the Gaussian 98 program in order to find their structures and energies. The structures of the transition states between pairs of conformers were also found. The theoretical vibration spectra of the most stable 2,4-pentanedione enol form and the diketoform are discussed in detail. Several interconversions were studied from the standpoint of the solvent influence on the intramolecular H-bond strength and energy barriers.

- 22 В. Б. Делчев**, Х. Микош, “Сравнително разглеждане на амин-иминната тавтомерия в аденин с метода на Хартри-Фок и теорията за функционала на плътността” (2005) *Научни трудове, Пловдивски университет*, **32:5**, 95-100.

Abstract. Four tautomers of adenine (N9H-amino, N9H-imino, N7H-amino, and N7H-imino) were studied by means of Hartree-Fock method. Their structural and electron properties were compared to those obtained by B3LYP/6-311G(d,p) calculations. The transition states of the tautomeric conversions were found in the gas phase and in solvents acetonitrile and chloroform (using Onsager’s model). In some cases the energy barriers of the conversions were found to be higher than those in the gas phase.

- 23 В. Б. Делчев**, Х. Микош, “Изучаване на кето-енолната тавтомерия в малонилцистеамина с помощта на теорията за функционала на плътността” (2005) *Съюз на учените в България – Пловдив, серия Б. Естествени и хуманитарни науки*, **V**, 7-12.

Abstract. The mechanism of the keto-enol transformation of malonylcysteamine was studied at the B3LYP level of theory using 6-31++G(d) and 6-31+G(d) basis functions. Both basis sets predicted almost equal values for thermodynamic, structural and vibration parameters. It was found that keto-enol transformation of malonylcysteamine has very high energy barriers in the gas phase.



- 26 V. B. Delchev, H. Mikosch, "Investigation of the intermolecular proton transfer in the supersystem adenine-methanol: a DFT level study" (2005) *Scientific researches of the Union of Scientists in Bulgaria – Plovdiv, Series C. Technics and Technologies, Balkan Conference of Young Scientists*, 16-18 June 2005, **5**, 303-308.**

Abstract. Two tautomeric forms of adenine are the objects of the current paper: imine and amine tautomer. Their geometries and electronic structures were studied at the B3LYP/6-311G(d,p) level of theory. The four tautomers were involved in four supersystems with H-bonded methanol. The stability of the supersystems, the thermodynamic and kinetic properties of the intermolecular proton transfers were studied in order to explain one different approach for a keto-enol conversion in adenine, namely the proton transfer assisted by small protic molecules.

- 29 V. B. Delchev, H. Mikosch, "DFT study of the gas phase proton transfer in guanine assisted by water, methanol and hydrogen peroxide" (2006) *Journal of Molecular Modeling*, **12:2**, 229-236. IF = 1.384**

Abstract. A computational study of hydrogen-bonded complexes between the oxo-/hydroxo-amino N7/9H tautomers of guanine and water, methanol and hydrogen peroxide has been performed at the B3LYP/6-31+G(d) level of theory. The mechanisms of the water-, methanol-, and hydrogen peroxide-assisted proton transfers in guanine were studied and compared with the intramolecular proton transfer in guanine in the gas phase. It was found that the assisted proton transfers pass through about 3 times lower energy barriers than the energy barriers found for isolated guanine tautomers.

- 32 И. Г. Щерев, В. Б. Делчев, "Теоретично изследване на изомерните превръщания на урацил в газова фаза" (2006) *Научни трудове на ПУ*, **34:5**, 105-111.**

Abstract. Nine isomers (tautomers and conformers) of uracil were studied at the B3LYP and MP2 theoretical levels, using the basis set 6-311++G(d,p). The transition states of the isomerizations were found, each as a first order saddle point on the reaction energy hypersurface. The crystal structure of uracil was investigated experimentally (X-ray powder analysis) and theoretically using a molecular mechanics force field. A cluster of four uracil molecules, resembling a part from its crystal lattice, was minimized by means of the PCMODEL program. The experimental and theoretical spacing between the crystal lattice planes are correspondingly $d=3.135 \text{ \AA}$ and $d=3.180 \text{ \AA}$.

- 33 V. B. Delchev, H. Mikosch, "Theoretical study of the intermolecular H-bonding and intermolecular proton transfer between isocytosine tautomeric forms and R,S-lactic acid " (2007) *Journal of Molecular Modeling*, **13:1**, 19-28. IF = 1.669**

Abstract. Eight H-bonded complexes between isocytosine (*isoC*) tautomeric forms and R/S-lactic acid (LA) have been studied at the B3LYP and HF levels of theory using 6-31+G(d) basis set. The energy barriers of the intermolecular proton transfers were also estimated as the results showed that they are several times lower than those of the intramolecular proton transfers of *isoC* in the gas phase. Furthermore, the energy barriers of the tautomerizations in which the carboxylic H-atom takes part are several times lower than those in which the LA OH group assists the proton transfer.

- 35 V. B. Delchev, I. G. Shterev, "Theoretical study of the tautomeric forms of acetylacetone: HF and DFT level of investigation" (2007) *Bulgarian Chemical Communications*, **39:2**, 98-105.**

Abstract. Theoretical calculations of the tautomeric forms of acetylacetone were performed at the HF and B3LYP levels using the basis sets 6-31G and 6-311G including a different number of diffuse and polarization functions. The single-point computations of the enol form resulting from the electron diffraction analysis predicted one imaginary frequency in its vibrational spectrum. This vibrational



motion could be considered as a single oscillation, which cannot be determined by diffraction analysis. It was shown that the single-point and optimization energies are not sensitive to the inclusion of second diffuse functions of hydrogen atoms. However, these energy parameters are much more sensitive to the inclusion of polarization functions.

- 36 V. B. Delchev, G. T. Delcheva, “DFT Study of the Oxaloacetic acid Condensation – the First Step of the Citric Acid Cycle” (2007) *Journal of Structural Chemistry*, **IF = 0.481** 48:4, 615-622.**

Abstract. The mechanism of acylation of oxaloacetic acid (OA) with acetyl-CoA was studied at the DFT level using the basis functions 6-311G(d,p) and different numbers of diffuse functions. Four mechanisms are considered in this study. It is found that the most probable mechanism, in the approximation of isolated molecules, starts with the enol forms of oxaloacetic acid and acetylcystamine (final fragment from acetyl-CoA). The mechanisms are commented from the viewpoint of their thermodynamics. The calculations and UV/VIS spectroscopic analysis of OA showed that the enol form of the compound is available in ethanol, water and diethyl ether. The higher stability of the OA enol form (compared to the stability of the ketoform) was also reconfirmed by its experimental IR spectrum. The energy barrier of the enolization reaction of OA was calculated to be very high.

- 37 V. B. Delchev, I. G. Shterev, H. Mikosch, N. T. Kochev, “Investigation of the intermolecular proton transfer in the supersystems adenine – methanol/ethanol/i-propanol: MP2 and DFT levels study” (2007) *Journal of Molecular Modeling*, **IF = 1.669** 13:9, 1001-1008.**

Abstract. Twelve H-bonded supersystems constructed between the adenine tautomers and methanol, ethanol, and i-propanol were studied at the B3LYP and MP2 levels of theory using 6-311G(d,p) and 6-311++G(d,p) basis functions. The thermodynamic parameters of the complex formations were calculated in order to estimate the exact stability of the supersystems. It was proven that the calculated energy barriers of the alcohol-assisted proton transfers are about 60% lower than those of the intramolecular proton transfers in adenine found earlier (*Gu and Leszczynski in J Phys Chem A 103:2744–2750, 1999*).

- 39 V. B. Delchev, M. Nenkova, “Theoretical modeling of the ground state intramolecular proton transfer in cytosine: DFT level study” (2008) *Acta Chimica Slovenica*, **IF = 0.909** 55, 132-137.**

Abstract. Five isomers of cytosine and their mutual interconversions were studied theoretically at the B3LYP level using basis sets 6-31G and 6-311G and a different number of polarization and diffuse functions. It was demonstrated that the canonic aminooxo tautomer of cytosine is the most stable one. However it has a non-planar geometry. It was shown that the energies and energy barriers of the studied systems are sensitive to the inclusion of polarization functions in the basis set, but they have lesser sensitivity toward inclusion of diffuse functions.

- 40 V. B. Delchev, I. G. Shterev, H. Mikosch, “Theoretical investigation (DFT and MP2) of the intermolecular proton transfer in the supersystems uracil-(H₂O)_n and uracil-(CH₃OH)_n (n=1,2)” (2008) *Monatshefte für Chemie*, **IF = 1.426** 139, 349-362.**

Abstract. Twelve binary and eight ternary H-bonded systems between uracil and water/methanol were investigated at the B3LYP and MP2 theoretical levels using 6-31+G(d) basis functions. The binary and ternary systems that contain the hydroxo-uracil tautomer H-bonded with water and methanol were found to be the most stable complexes. The calculated energy barriers of the intermolecular proton exchange showed that the methanol molecule provokes larger reduction of the energy barrier of the intermolecular proton exchange reactions than the water molecule.



- 41 V. B. Delchev, I. G. Shterev, "Ground state intermolecular proton transfer in the supersystems thymine-(H₂O)_n and thymine-(CH₃OH)_n, n=1,2: a theoretical study" IF = 2.336**
Journal of Molecular Modeling (2009) **15:4**, 411-419

Abstract. Twelve binary and eight ternary supersystems between thymine and methanol, and water were investigated in the ground state at the B3LYP and MP2 levels of theory using B3LYP/6-311++G(d,p) basis functions. The thermodynamics of complex formations and the mechanisms of intermolecular proton transfers were clarified in order to find out the most stable H-bonded system. It was established that the energy barriers of the water/methanol-assisted proton transfers are several times lower than those of the intramolecular proton transfers in the DNA/RNA bases. The X-ray powder spectra of thymine, and this precrystallized from water and methanol showed that water molecules are incorporated in the crystal lattice of thymine forming H-bridges between thymine molecules.

- 42 I. G. Shterev, V. B. Delchev, "Theoretical investigation of the intermolecular H-bonding and proton transfer in cytosine assisted by water and methanol" (2009) IF = 1.312**
Monatshefte für Chemie, **140:11**, 1381-1394.

Abstract. The investigation is devoted to the study of the electronic structure of H-bonded complexes of cytosine tautomers with water and methanol molecules. The stability of those "supersystems" (aggregates) was estimated by the calculated bonding parameters ΔE and ΔE_b . The energy barriers of the water / methanol-assisted tautomeric conversions were calculated (intermolecular proton transfer), and the electronic structures of the transition states were studied. Each transition state of the proton transfer reaction was determined as a first order saddle point on the potential energy surface (of the full coordinate hyperspace) of the reaction. The crystal structure of the tetramer of cytosine monohydrate was also studied. Its structure was found to be very close to a conical intersection.

- 43 S. Georgiev, R. Karaminkov, S. Chervenkov, V. Delchev, H. J. Neusser, "Mass-Analyzed Threshold Ionization Spectroscopy of 2-Phenylethanol: Probing of Conformational Changes Caused by Ionization" (2009) IF = 2.899**
Journal of Physical Chemistry A, **113:44**, 12328-12336.

Abstract. The vibrational structure of the ionic ground state of different conformers of the biologically relevant molecule 2-phenylethanol has been investigated by combination of two-photon two-color mass-analyzed threshold ionization spectroscopy (MATI) and quantum chemical calculations at M05, MP2, and coupled cluster (CC) levels of theory with extended basis sets. MATI spectra recorded via gauche vibronic bands are with poor structure and increasing background, whereas the ones measured via vibronic bands of the anti conformers feature well-resolved vibronic structure in the cation. Ab initio computations predict three stable conformers for the 2-phenylethanol cation out of five initial neutral structures. None of the theoretical structures in the cation features a nonclassical OH $\cdots\pi$ hydrogen bond in conjunction with the analysis of the MATI spectra. This provides clear evidence that the OH $\cdots\pi$ hydrogen bond stabilizing the lowest-energy gauche conformer in the neutral breaks upon ionization.

- 44 V. B. Delchev, "Semi-diabatic PESs of the photo-induced rotations of the stable enol form of acetylacetone around the C=C and C-O bonds: TD B3LYP level study" (2010) IF = 1.312**
Asian Chemistry Letters, **14:3**, 267-272.

Abstract. Four planar rotamers of the enol form of acetylacetone were theoretically studied at the TD B3LYP/cc-pVDZ level of theory with respect to their mutual photoinduced conversions through the PES of the bright $^1\pi\pi^*$ state. A barrierless and radiatioless relaxation of the excited-state through a conical intersection (CI) to the ground-state minima of all planar rotamers was found. This finding implies an ultrafast deactivation of the excited $^1\pi\pi^*$ state of each rotamer with generation of almost all



four rotamers. Some of them can not be obtained thermally because of high energy barriers on the So surface, especially these related to the rotation around the double C=C bond.

- 45 V. B. Delchev**, “Computational (DFT and TD DFT) study of the electron structure of the tautomers / conformers of uridine and deoxyuridine and the processes of intramolecular proton transfers” (2010) *J. Mol. Mod.*, **16:4**, 749-757. **IF = 1.871**

Abstract. Six uridine and six deoxyuridine isomers were studied at the B3LYP and TD B3LYP theoretical level and 6-31+G(d) basis function. The stability and the excited states of the isomers were studied in order to clarify some known experimental data. It was established that the rotation of the oxo uracil ring in uridine is energetically more likely to occur in the excited state than in the ground state, driven by the bright ${}^1\pi\pi^*$ state and the dark charge transfer ${}^1n\pi^*$ state. Very high energy barriers (on the So) were found for thermal intramolecular proton transfer processes.

- 46 V. B. Delchev**, W. Domcke, “Cyclodimerization of DNA and RNA bases: *Ab initio* study of the cyclodimerization of the uracil dimer through a butane-like conical intersection” (2010) *High Performance Computing in Science and Engineering, Garching/Munich 2009*, Part **7**, 709-718, **DOI:** 10.1007/978-3-642-13872-0_59 (Springer)

Abstract. The mechanism of the photo-induced cyclodimerization of uracil through a butane-like conical intersection was studied with the CASPT2, CC2, and DFT ab initio electronic-structure methods. The linear-interpolation-in-internal-coordinates (LIIC) approach was applied to construct reaction paths and potential-energy profiles connecting reactants and products. The structures of the *cis-syn* cyclodimer, the S_0/S_1 conical intersection and the stacked dimer of uracil were optimized at the CASSCF level. Our calculations support a qualitative mechanistic picture of the relaxation mechanisms of the ${}^1\pi\pi^*$ state of the cyclodimer and the stacked dimer of uracil through a S_0/S_1 conical intersection.

- 47 V. B. Delchev**, A. L. Sobolewski, W. Domcke, “Comparison of the non-radiative decay mechanisms of 4-pyrimidinone and uracil: an ab initio study” (2010) *Phys. Chem. Chem. Phys.*, **12**, 5007 – 5015. **IF = 3.453**

Abstract. We performed a comparative theoretical study of the relaxation mechanisms of the excited states of uracil and 4-pyrimidinone with the CASSCF, CASPT2, and CC2 ab initio methods. The calculated vertical excitation energies agree with the experimental UV absorption maxima of the two compounds. Three low-lying conical intersections between the S_0 and S_1 states (one for uracil, two for 4-pyrimidinone) are established. They are accessible from the Franck–Condon region of the ${}^1\pi\pi^*$ state through out-of-plane deformations related to C=C (for uracil) or C=N (for 4-pyrimidinone) torsions of the heterocyclic ring. These conical intersections mediate the radiationless deactivation of the compounds after excitation of the lowest ${}^1\pi\pi^*$ state. The relaxation of the ${}^1\pi\pi^*$ state of 4-pyrimidinone via C=C twisting is hindered by a barrier. The relaxed scan of the C=N double-bond twisting of 4-pyrimidinone indicates that the formation of the Dewar form may represent a photochemical channel in 4-pyrimidinone. This fact is detrimental for the photostability of 4-pyrimidinone, since the Dewar form is separated by a high potential-energy barrier from the canonical form of 4-pyrimidinone on the ground-state potential-energy surface, which prevents a thermal back-reaction. The investigation of the vertical excitation energies and the reaction paths shows that 4-pyrimidinone is less photostable than uracil.

- 48 V. B. Delchev**, “Photoinduced conformational transformation of the hydroxy form of uridine and deoxyuridine and hydrogen detachment in oxo and hydroxy tautomers of the compounds: a computational study” (2010) *Monatshefte für Chemie*, **141:10**, 1153 –1157. **IF = 1.356**



Abstract. In this research we studied the mechanisms of photoinduced conformational transformation of hydroxyl forms of (deoxy)uridine, which have been found to be accessible in aqueous solution. The mechanisms were compared with those for the oxo forms of (deoxy)uridine studied recently. The mechanisms of photoinduced proton detachment in oxo and hydroxy forms of (deoxy)uridine were also studied. These mechanisms are driven by the repulsive $^1\pi\sigma^*$ state.

- 49 V. B. Delchev**, “Face-to-back” photo-cyclodimerization of the malonaldehyde enol form with the strong intramolecular H-bond: A TD DFT theoretical study **IF = 1.288** (2010) *J. Mol. Struct. THEOCHEM*, **958**, 101-105.

Abstract. In this investigation we discussed one possible mechanism of the photoinduced cyclodimerization of two malonaldehyde molecules to form the “face-to-back” cyclodimer. Linear interpolation in internal coordinates approach was applied to study the excited-state relaxation mechanisms at the TD DFT level with aug-cc-pVDZ basis functions. It was found that the formation of the cyclodimer occurs through the first $^1\pi\pi^*$ excited state which has a charge transfer character. We also found a radiationless relaxation path of the $^1\pi\pi^*$ excited state mediated by a S_0 - S_1 conical intersection.

- 50 V. B. Delchev**, “The shape of the conical intersections of monohydrated pyrimidine bases cytosine, uracil, and thymine: a theoretical study” (2011) **IF = 1.532** *Monatshefte für Chemie*, **142:3**, 251-260.

Abstract. Three conical intersections of monohydrated cytosine, uracil, and thymine were found between the S_0 and S_1 states. The pyrimidine bases in these conical intersections have unusual shape with rather distorted aromatic rings caused by the strong interactions between the pyrimidines and the water molecule. The conical intersections of uracil and thymine monohydrates have structures with considerable out-of-plane deviation of one of the carbonyl groups. The conical intersection of cytosine monohydrate showed a ring cleavage of the N_1 - C_2 bond, while the NH_2 group is almost perpendicular to the aromatic ring. The three conical intersections show a tendency to form Dewar forms. Thus, in the theoretical study we included the possible Dewar forms of the monohydrated pyrimidine bases closely related to the structures of the conical intersections.

- 51 V. B. Delchev**, Ivan G. Shterev, “Local characterization of the conical intersection of the cyclodimerization reaction of the malonaldehyde enol form: an *ab initio* study” (2011) *Asian Chemistry Letters*, **15:1,2**, 59-66.

Abstract. In the current theoretical study we performed CASSCF-calculations in order to characterize local properties of the low-lying S_0 - S_1 conical intersection mediating the radiationless relaxation of excited states of the [2+2] cyclodimerization reaction of two molecules of methanol (face-to-back position). The constructed adiabatic and diabatic potential energy surfaces revealed the nature of this conical intersection and confirmed its role in the excited state relaxation processes of two systems: stacked dimer and cyclodimer. The structures of the stacked dimer, cyclodimer and the conical intersection as well as the normal modes of the stable minima were optimized/calculated at the CASSCF level of theory. The branching space vectors were also calculated at the same level.

- 52 V. B. Delchev**, Ivan G. Shterev, “Photoinduced disruption of the strong intramolecular H-bond in the enol form of acetylacetone: mechanisms of radiationless decay” (2011) *Computational and Theoretical Chemistry*, **967**, 152-159. **IF = 1.437**

We propose mechanisms which describe the photoinduced disruption of the intramolecular H-bond in the stable enol form of acetylacetone. The study was performed with the second-order approximate coupled cluster singles and doubles model CC2. The basis set aug-cc-pVDZ was applied. The excited-state reaction paths of the rotations around C-C, C=C and C-O bonds were investigated using both



coordinate-driven (relaxed scan) and linear interpolation in internal coordinates (LIIC) approaches. We show that the $^1\pi\pi^*$ excited states of the rotations around the C=C double bond relax in, a completely barrierless manner, to the ground state via S_0 - S_1 conical intersections. This is the main relaxation channel of the excited states associated with the disruption of the strong H-bond in the enol form of acetylacetone. The C-C and C-O rotations did not show such mechanisms.

- 53** R. Karaminkov, S. Chervenkov, **V. Delchev**, H. Neusser, "High-Resolution Mass-Selective UV Spectroscopy of Pseudoephedrine: Evidence for Conformer-Specific Fragmentation" (2011) *J. Phys. Chem. A*, **115:34**, 9704–9713. **IF = 2.946**

Abstract. Using resonance-enhanced two-photon ionization spectroscopy with mass resolution of jet-cooled molecules, a low-resolution $S_1 \leftarrow S_0$ vibronic spectrum of pseudoephedrine was recorded at the mass channels of three distinct fragments with $m/z = 58, 71, \text{ and } 85$. Two of the fragments, with $m/z = 71$ and 85 , are observed for the first time for this molecule. The vibronic spectra recorded at different mass channels feature different patterns, implying that they originate from different conformers in the cold molecular beam, following conformer-specific fragmentation pathways. Highly resolved spectra of all prominent vibronic features were measured, and from their analysis based on genetic algorithms, the molecular parameters of the conformers giving rise to the respective bands have been determined. Comparing the experimental results with those obtained from high-level ab initio quantum chemistry calculations, the observed prominent vibronic bands have been assigned to originate from four distinct conformers. The conformers are separated into two groups that have different fragmentation pathways determined by the different intramolecular interactions.

- 54** **В. Б. Делчев**, И. П. Иванова, "Изследване на реакционните пътища на възбудените състояния при NH- и CH- дисоциация на барбитуровата киселина" (2011) *Сборник доклади, Юбилейна национална научна конференция с международно участие "Човекът и Вселената"*, СУБ-Смолян, първо издание, 6-8 Октомври 2011, 379-383.

Abstract. In the current research we present reaction mechanisms of the NH- and CH-dissociation of the tautomeric form of barbituric acid. The calculations were performed at the B3LYP (TD) level of theory with the aug-cc-pVDZ basis set. The results show that the NH-dissociation of barbituric acid occurs through the repulsive $^1\pi\sigma^*$ excited state. This is a part of so-called PIDA (photoinduced dissociation-association) mechanism. The excited-state reaction path of the bright $^1n\sigma^*$ excited state runs almost parallel to this of the $^1\pi\sigma^*$ excited state. We concluded that this is a channel to populate the dark $^1\pi\sigma^*$ excited state of barbituric acid. The CH-dissociation seems to have no practical contribution to the photochemical tautomerization of barbituric acid.

- 55** P. B. Kancheva, **V.B. Delchev**, "Excited-state reaction paths of cytosine and isocytosine: C=O elongation" (2011) *Научни трудове ПУ*, **38:5**, 71-80.

Abstract. We investigated the excited-state reaction paths for the C=O elongation in the most stable oxo-amino tautomers of cytosine and isocytosine. They were studied at the B3LYP (TD) level of theory and aug-cc-pVDZ basis functions. As expected for this kind of reactions no conical intersections S_0 - S_1 were found for both compounds. We explained the ps-relaxation of cytosine with the population of the $^1n\sigma\pi^*$ excited state via conical intersection $^1n\sigma\pi^*/^1\pi\pi^*$ and subsequent fluorescence to the S_0 state at $C=O = 1.443 \text{ \AA}$. For isocytosine we found a channel for the population of the $^1\pi\sigma^*$ excited state, which would contribute to the photochemical dissociation of this compound. This is the first step for the formation of the hydroxo tautomer of isocytosine.

- 56** R. Bakalska, **V. B. Delchev**, "Photoinduced tautomerism of 2-thiobarbituric acid studied by theoretical and experimental methods" (2012) *Acta Chim. Slov.*, **59**, 75-82. **IF = 1.328**



Abstract. Combined, theoretical and experimental, investigation was performed to study the mechanism of the photoinduced tautomerism of 2-thiobarbituric acid (TBA). The irradiation of the solution of TBA in polar aprotic solvent with UV light (maximum at 366 nm) showed oxo-hydroxy photoisomerization of the triketo form of TBA to the hydroxy-imino tautomer. The studied mechanisms (TD DFT) of the photoinduced NH and OH dissociations in the keto and enol tautomer revealed that the proton detachment in the triketo tautomer occurs in the bright $^1n\sigma^*$ excited state. In the hydroxy-imino tautomer this mechanism is driven by the repulsive $^1\pi\sigma^*$ excited state. The excited-state relaxation mechanisms occur by low-lying S_0 - S_1 conical intersections.

- 57** I. G. Shterev, **V. B. Delchev**, "Excited-state deactivation of the monohydrated complexes of cytosine, uracil and thymine through S_0/S_1 conical intersections" **IF = 1.532** (2012) *Monatshefte für Chemie*, **143**, 763-770.

Abstract. The nucleobases cytosine, uracil, and thymine and their H-bonded complexes with one molecule of water were studied at the CC2/aug-cc-pVDZ level of theory. The excited-state deactivation mechanisms through the conical intersections S_0/S_1 were investigated. It was found that the $^1\pi\pi^*$ excited states of cytosine, the hydroxy tautomer of uracil, and the hydroxy tautomer of thymine relax nonradiatively to the ground state S_0 . However, only monohydrated and anhydrous thymine do not have energy barriers of the $^1\pi\pi^*$ excited-state reaction paths. The photophysical reaction of monohydrated thymine could proceed in two directions on the S_0 surface.

- 58** **V. B. Delchev**, I. P. Ivanova, "Theoretical study of the excited-state reaction paths of the OH- and NH-dissociation processes in barbituric acid" (2012) *Monatshefte für Chemie*, **143**, 1141-1150 **IF = 1.532**

Abstract. We studied the OH and NH dissociation mechanisms of eight tautomers of barbituric acid via excited states. The theoretical research was performed at the TDDFT level of theory (B3LYP). It was found that all mechanisms pass through the repulsive $^1\pi\sigma^*$ excited state whose excited-state reaction paths showed conical intersections S_0 - S_1 . Some OH dissociation mechanisms showed barrierless $^1\pi\sigma^*$ reaction paths which indicate an ultrafast relaxation of the $^1\pi\sigma^*$ excited states to the ground state. The study of the NH dissociation mechanisms revealed that almost all $^1\pi\sigma^*$ reaction paths show low energy barriers and minima before the conical intersections S_0 - S_1 .

- 59** R. I. Bakalska, **V. B. Delchev**, "Comparative study of the relaxation mechanisms of the excited states of cytosine and isocytosine" (2012) *J. Mol. Mod.*, **18**, 5133-5146. **IF = 1.797**

Abstract. An experimental and theoretical investigation was performed to study the photostability of cytosine and isocytosine. The experimental UV irradiation of acetonitrile solutions of the two compounds showed that the amino-oxo tautomer of cytosine is photostable while the amino-oxo tautomer of isocytosine tautomerizes to the amino-hydroxy form. The theoretical investigations were carried out at the CC2 level of theory. They were performed to explain the experimental observations. It was found that the $^1\pi\pi^*$ excited states of the ring deformation mechanisms of cytosine and isocytosine relax (internal conversion) to the ground states of the amino-oxo forms of the compounds. We propose a channel for the radiationless deactivation of the repulsive $^1\pi\sigma^*$ excited state of the amino-oxo form of isocytosine to the ground state of the amino-hydroxy tautomer.

- 60** И. Г. Щерев, И. И. Тошев, **В. Б. Делчев**, "Теоретично изучаване на водородно свързаните комплекси на серотонина с n молекули вода (n=1, 2, 3, 4, 5, 6 и 7)" (2012) *Научни трудове на УХТ*, **LIX**, 389-394.

Abstract. Ten H-bonded complexes between serotonin (5-hydroxy-tryptamine) and water were studied at the B3LYP level of theory, using the aug-cc-pVDZ basis set. The thermodynamic analysis showed



that the most stable complex between serotonin and water is se_4. The calculated energies and bonding parameters confirm that the most stable H-bonded complex is formed by means of the intermolecular H-bond between N-atom of -NH₂ group of serotonin and H-atom from water molecule (-H₂N...H-OH).

- 61** И. Г. Щерев, Н. Т. Николов, В. Б. Делчев, “Ефекти на хидратираната вода върху вертикалните енергии на възбуждане на водородно свързаните комплекси на серотонина с вода” (2012) *Научни трудове на УХТ*, **LIX**, 636-640.

Abstract. 5-hydroxytryptamine (serotonin, 5-HT) is a hormone and neurotransmitter in the central nervous system. The conformation flexibility of the alkyl lateral chains in 5-HT plays a crucial role in his association with the receptors. The optimization of geometry of serotonin and his complexes with water was performed on B3LYP theoretical level using the aug-cc-pVDZ basis set. For the serotonin and for each one complex the vertical excitation energies were calculated. The connection between H-bonded water and the processes of excitation was established.

- 62** V. B. Delchev, “Excited-state relaxation paths of oxo / hydroxy and N9H / N7H tautomers of guanine: a CC2 theoretical study” (2013) *J. Mol. Mod.*, **19**, 2299-2308. **IF = 1.984**

Abstract. We performed a theoretical investigation, at the CC2/aug-cc-pVDZ level, of the ring-deformation mechanisms of four guanine tautomers (oxo, hydroxy, N9H, and N7H). The study showed that the optimized conical intersections S₀/S₁ are accessible through the ¹ππ* excited states of tautomers. The optimized conical intersections S₀/S₁, which show deformation at the pyrimidine ring, have high energies. This means that the relaxations of the ¹ππ* excited states via internal conversion are disfavored. For two tautomers we found crossing points ¹ππ*/¹πσ* of the excitedstate reaction paths, revealing the possibility of a population of the ¹πσ* excited state by the ¹ππ* excited state.

- 63** В. Б. Делчев, “Конични сечения S₀/S₁ при гуанина, свързани с деформация на пуриновия пръстен” (2013) *Сборник доклади на Юбилейната национална научна конференция с международно участие “Традиции, посоки, предизвикателства”, Смолян 19-21 октомври 2012*, **III**, 203-207.

Abstract. Guanine is a nucleic acid base which exists in several tautomeric forms, but only one (oxo) of them has considerable biological functions since it participates in the processes of transcription and encoding of genetic information. This compound is rather photostable exposed to UV light. In order to explain the high photostability of oxo guanine we performed CC2 and CASSCF calculations to find conical intersections S₀/S₁ and the ¹ππ* excited-state equilibrium geometries of two oxo tautomers (N7/9H). The found conical intersections and the modeled adiabatic PESs revealed the pathways for the radiationless relaxations of the S₁ excited states to the ground states. These conical intersections show deformations of the purine ring at the amino group. So far, such conical intersections have not been reported.

- 64** V. B. Delchev, “Comparative study of the O...H...O proton transfer in the enol form of a single acetylacetone molecule and acetylacetone incorporated in β-cyclodextrin: a theoretical investigation” (2013) *Monatshefte für Chemie*, **144**, 1153-1158. **IF = 1.629**

Abstract. We performed a comparative theoretical study (at the B3LYP/6-31G(d) level) of the H-exchange reaction of acetylacetone and of acetylacetone incorporated in β-cyclodextrin. The investigation showed that the incorporation of acetylacetone in β-cyclodextrin leads to weakening of the strength of the intramolecular H-bond and disturbance of the planar geometry of the enol form of the compound. Moreover, the H-exchange in single acetylacetone occurs, in a barrierless manner, through the ¹ππ* excited state. The same reaction of acetylacetone incorporated in β-cyclodextrin passes through



energy barriers in the excited and the ground state. In other words, the inclusion of the acetylacetone in β -cyclodextrin hinders the H-exchange reaction (thermal and photochemical).

- 65** V. B. Delchev, W. Domcke, “Ab initio study of the cyclodimerization of uracil through butane-like and oxetane-like conical intersections” (2013) *J. Photochem. Photobiol. A: Chemistry*, **271**, 1-7. **IF = 2.416**

Abstract. In the present work we explored the mechanisms of the formations of the uracil cyclobutane and oxetanecyclodimers using ab initio methods through excited states and the S_0 - S_1 conical intersections. The excited-state reaction paths showed that the $^1\pi\pi^*$ excited states of the stacked dimers can relax, in a barrierless manner, to the ground states via S_0 - S_1 conical intersections. We found that the destruction of the cyclodimers occurs through $^1\pi\pi^*$ excited states and the same S_0 - S_1 conical intersections. In other words, the formation and the destruction of the uracil cyclodimers are competitive reactions initiated by UV light. Excited-state reaction paths show that the production of the cyclobutane dimer is much more favorable than the oxetane adduct.

- 66** И. Щерев, М. Говедаров, В. Делчев, “Сравнително разглеждане на вътрешномолекулния и (ин)директния междумолекулен протонен пренос в тимина: DFT изследване” (2013) *Научни трудове (УХТ)*, **LX**, 734-738.

Abstract. The mechanisms of the reactions of intra and direct/indirect proton transfer in thymine cluster with one and eight water molecules were investigated at the DFT level of theory (B3LYP/aug-cc-pVDZ). The transition states (TS) standing on the ground state reaction path between the oxo and hydroxy forms were found and the energy barriers of the reactions were estimated.

- 67** И. Щерев, Д. Димитрова, В. Делчев, “Сравнително DFT изследване на механизма на N-H фотодисоциация в oxo формата на барбитуровата киселина в газова фаза и разтворител етанол” (2013) *Научни трудове (УХТ)*, **LX**, 679-683.

Abstract. The mechanism of the N-H photodissociation in the oxo form of barbituric acid was investigated comparatively in the gas phase and in ethanol solution. The investigations were carried out with the tools of the computational chemistry: at the BLYP (TD) theoretical level using aug-cc-pVDZ basis functions. The excited-state reaction paths of the N-H photodissociations, as obtained by the relaxed-scan approach, were compared. The results showed that the driven state, leading to a S_0/S_1 conical intersection, is the $^1n\sigma^*$ one. In the gas phase no barrier on the excited-state reaction path of this state was found whereas in ethanol solution a barrier of about 0.4 eV is found.

- 68** I. G. Shterev, V. B. Delchev, “Solvent influence on the excited states of the oxo form of barbituric acid and the mechanisms of the out-of-plane non-radiative elongation of the out-of-plane nonradiative elongation of the N-H bond: a comparative theoretical and experimental study” (2014) *Spectrochimica Acta Part A*, **125**, 384-390. **IF = 2.353**

The solvent influence on the excited states, emission and absorption energies of the oxo form of barbituric acid was studied with experimental (UV and fluorescence spectra) and theoretical methods. The excited-state reaction paths of the out-of-plane elongation of the N-H bond of the oxo form of barbituric acid were also investigated (TD DFT level) to the conical intersections mediating internal conversions to the ground state. The $^1n\sigma^*$ excited state was found to be the driven electronic state. We found that the increase of the polarity of the solvent reduces the $^1n\sigma^*$ excited state decay rate through a non-planar conical intersection and increases its energy. Thus, solvents with higher polarity disfavor the non-radiative decay through conical intersections.



- 69** C. Rabong, C. Schuster, T. Liptaj, N. Prónayová, **V. B. Delchev**, U. Jordis, J. Phopase, “NXO beta structure mimicry: an ultrashort turn/hairpin mimic that folds in water” (2014) *RSC Advances*, **4**, 21351-21360. **IF = 3.840**

Abstract. We report the first application of NXO-pseudopeptides for β -turn mimicry. Incorporating the prolinederived NProO peptidomimetic building block, a minimal tetrapeptide β -hairpin mimic has been designed, synthesized and its solution structure elucidated. Emulating a natural proline–glycine β -turn, evidence from NMR, molecular modeling and CD suggests the formation of two rapidly interconverting hairpin folds in water, methanol and dimethyl-sulfoxide at room temperature, displaying the praline nitrogen amide bond in either cis or trans arrangement. The NProO-modified hairpin features peptidic backbone dihedrals Φ , Ψ characteristic of natural proline-containing turns composed of α -amino acids only. Taken together, the observed folding behavior and inherently high designability render the NProO motif a building block for β -structure elaboration in aqueous medium.

- 70** **V. B. Delchev**, “Xanthine and hypoxanthine: in a search for conical intersections S_0/S_1 connected with deformations of pyrimidine residue of the purine ring” (2014) *Bulg. Chem. Commun. (Special Issue)*, **46**, 203-208. **IF = 0.201**

Abstract. The oxo N9H tautomers of xanthine and hypoxanthine were studied theoretically at the CC2/aug-cc-pVDZ level in order to find conical intersections S_0/S_1 , which show deformations of the pyrimidine rings. The conical intersections were characterized locally by adiabatic surfaces constructed on the narrow grid. The accessibility of the conical intersections from the excited state was also implied.

- 71** **V. B. Delchev**, K. B. Gavazov, I. G. Shterev, “Ground- and excited-state stability of the conformers of 3,5-dinitrocatechol and its complexes with W(VI) and V(V): combined theoretical and experimental study” (2014) *J. Mol. Mod.* **20**, 2549(8) **IF = 1.736**

Abstract. We performed a theoretical and experimental study of the (photo)stability of 3,5-dinitrocatechol (DNC) and its complexes with W(VI) and V(V). The investigation showed that the irradiation of DNC is accompanied with a parallel proton migration from the hydroxy group to the neighboring NO_2 group, which results in a large Stokes shift of the absorption and emission bands. It was found that W(VI) forms more stable 1:2 complex than V(V). The complex is stable even under UV irradiation. The most stable $\text{W}^{\text{VI}}(\text{DNC})_2$ conformer is formed with two mutually perpendicular DNC molecules as ligands.

- 73** K. B. Gavazov, **V. B. Delchev**, G. K. Toncheva, Z. G. Georgieva, “Extraction-Spectrophotometric and Theoretical (Hartree-Fock) Investigations on a Ternary Complex of Iron(II) with 4-Nitrocatechol and 2,3,5-Triphenyl-2H-tetrazolium” (2015) *Russ. J. General Chem.*, **85:8**, 1945-1951 **IF₂₀₁₄=0.477**

Abstract. The complex formation and solvent extraction were studied in a system containing iron(II), 4-nitrocatechol (4NC), 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), water, and chloroform. Under the optimum conditions, the extracted complex has a composition of 1 : 1 : 2 (Fe–4NC–TTC) and could be represented with the formula $(\text{TT}^+)_2[\text{Fe}^{\text{II}}(\text{4NC}^{2-})(\text{OH})_2]$. Theoretical calculations were performed at the HF/3-21G* level in order to elucidate the geometric structure of the complex and electron distribution according to the crystal field theory. The results showed that the most stable configuration is tetrahedral low-spin structure. Some equilibrium constants (association, distribution, and extraction) and characteristics (absorption maximum, molar absorption coefficient, recovery factor, Beer’s law limits, etc.) concerning the application potential of the studied extraction–chromogenic system were determined.



- 74 I. G. Shterev, V. B. Delchev, "Excited-state deactivation channels via internal conversions in two position isomers of hydroxy-methyl-pyridine: a theoretical study" (2015) *J. Phys. Org. Chem.*, **28**, 681-689. **IF₂₀₁₄=1.380**

Abstract. Two position isomers of hydroxy-methyl-pyridine (3-hydroxy-2-methyl-pyridine and 2-hydroxy-3-methyl-pyridine) were studied theoretically at the BLYP level of theory in order to find mechanisms explaining the excited-state deactivations of isomers through ring puckering and "ethylene-like" conical intersections. The study aims also to clarify the mechanisms of the ground-state proton transfers. Three conical intersections S_0/S_1 for each isomer were found, which are accessible through the $^1\pi\pi^*$ excited states. In both isomers, there is a $^1\pi\pi^*$ excited-state reaction path, which leads, in a completely barrierless manner, to the one of the conical intersections S_0/S_1 .

- 75 K. B. Gavazov, V. B. Delchev, T. S. Stefanova, G. K. Toncheva, and K. K. Simitchiev, "Specific Features of Tetranitrotetrazolium Blue Chloride as an Extraction Reagent for Iron(III)" (2016) *Russ. J. General Chem.* – in press **IF₂₀₁₄=0.477**

Abstract. A liquid-liquid extraction-chromogenic system for Fe(III) containing 4-(2-thiazolylazo)resorcinol (TAR), [3,3'-(3,3'-dimethoxy-4,4'-biphenylene)bis[2,5-di(4-nitrophenyl)-2H-tetrazolium] chloride (Tetranitro-tetrazolium Blue chloride, TNBT), water, and chloroform was studied and compared with similar systems including other ditetrazolium salts (DTS), namely Neotetrazolium chloride (NTC), Blue Tetrazolium chloride, and Nitro Blue Tetrazolium chloride. The results show that the complex formed in the Fe(III)-TAR-TNBT system has different composition (1:3:2 vs. 1:2:1) and better extraction-spectrophotometric characteristics (fraction extracted of 98.6 % and molar absorptivity of $7.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at $\lambda = 495 \text{ nm}$). The proposed formula of the complex is $(\text{TNBT}^+)[\text{Fe}^{\text{III}}(\text{TAR}^{2-})_2]\{(\text{TNBT}^+)(\text{HTAR}^-)\}$. In this formula TNBT is in its monocationic form, $\text{TNBT}(\text{Cl})^+$, whose stability was established by Restricted Hartree-Fock (RHF) calculations and 3-21G* basis functions. At the same level were performed geometry optimizations as well as for NTC – a DTS which do not contain nitro- and methoxy groups. The obtained results (ground-state structures and total atomic charges) for TNBT, TNBT^+ , TNBT^{2+} , NTC and NT^{2+} were compared and discussed.

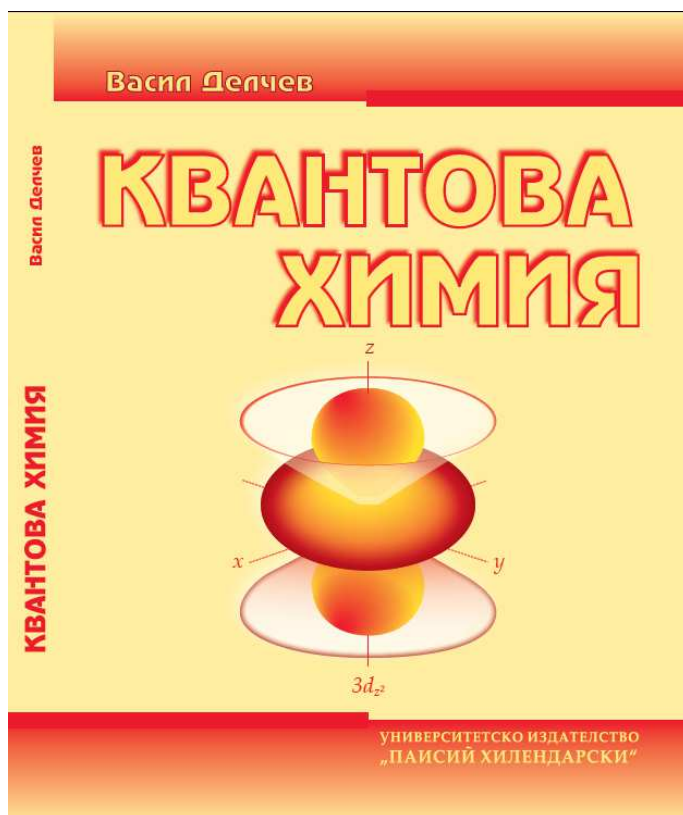
- 76 P. Kancheva, D. Tuna, V. B. Delchev, "Comparative study of radiationless deactivation mechanisms in cytosine and 2,4-diaminopyrimidine" (2016) *J. Photochem. Photobiol. A*, **321**, 266-274. **IF₂₀₁₄=2.495**

Abstract. We present a comparative computational CASPT2 and CC2 study of the deactivation mechanisms of electronically excited cytosine (Cyt) and 2,4-diaminopyrimidine (DAPy). A number of S_1/S_0 conical intersections exhibiting N-H bond elongation were optimized. These conical intersections are accessible from the Franck-Condon region along $^1\pi\sigma^*$ excited-state reaction paths. We also focus on the phototautomerism of DAPy and propose the photoinduced dissociation-association (PIDA) mechanism for this process. Supplementary experimental results on the UV irradiation of DAPy in acetonitrile solution show tautomerization to imino tautomers. By analyzing differences in the photophysics of the nucleobase Cyt and its analogue DAPy, this study provides new insight into the varying degrees of photostability between nucleobases and their close analogues.

Σ IF = 56.953

1. Учебник по Квантова химия, 2016 г.

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*Рецензент:* проф. д-р Аля Таджер

Учебникът „Квантова химия“ е съставен в съответствие с учебните програми на бакалавърските специалности в Химическия факултет на Пловдивския университет, които включват дисциплината като задължителна. Нуждата от списването на този учебник е продиктувана от актуализирането на учебните планове и програми за студенти бакалаври и от липсата на подходящи учебни помагала, които по достъпен начин да излагат иначе трудния материал по квантова химия. Авторът се е постарал да изясни на достъпен език основните положения на квантовата теория на атоми и молекули, както и теоретичните основи на молекулната симетрия. Учебникът е подходящ за студенти, докторанти и научни работници, провеждащи изследвания в областта на теоретичната химия.

Материалът в учебника е структуриран в осем глави. Обхванати са теориите, предхождащи квантовата механика, квантовата теория за строежа на едно- и многоелектронни атоми и теорията на химичната връзка. От учебника е изключена теорията на Бор, тъй като тя се изучава в курса „Обща и неорганична химия“.

Седма глава от учебника е „Молекулна симетрия“. Въпреки че симетрията на молекулите не е част от общата квантова теория, авторът е намерил за уместно да запознае студентите с елементите и операциите на симетрия, които са необходими за курса „Квантовохимични методи“ (за спец. „Компютърна химия“), който надгражда този по квантова химия. Молекулната симетрия е силен инструмент, с който се редуцира съществено компютърното време при провеждането на квантовохимични изчисления.

Списването на учебника е преди всичко компилативна работа, която предполага използването на голям брой литературни източници. В края на учебника е посочена използваната литература, както и някои интересни интернет връзки, свързани с темите от него.

Този учебник е посветен на моето семейство – съпругата ми и дъщеря ми, които в продължение на години проявяваха търпение и разбиране, без които настоящата книга не би била факт.

Горещо благодаря на рецензента на учебника проф. д-р Аля Таджер, чиито ценни съвети и препоръки помогнаха за подобряване на качеството на материала. Изказвам благодарност на колегите от катедра „Физикохимия“ на Пловдивския университет за подкрепата при списването и издаването на учебника.



Настоящият учебник е съставен в съответствие с програмата на бакалавърския курс по „Квантовохимични методи“, който се изучава през третата година на обучение от студентите, специалност „Компютърна химия“. Учебникът може да се използва също като помагало от докторанти и научни работници, които имат интереси в областта на изчислителната химия.

Материалът в учебника е структуриран в тринадесет глави, като с това авторът се е старал, ако не да обхване всички познати до сега квантовохимични методи, то да даде основните теории, които се използват в изчислителната химия. Към всяка глава, след заглавието, е включена кратка анотация на разглежданите методи и теории в нея. По такъв начин читателят ще може бързо и лесно да намери интересуващата го информация, без при това предварително да е запознат с конкретната теория.

На подходящи места в текста, авторът счита за необходимо да добави кратки биографични данни на някои известните учени с принос към изчислителната химия.

Голяма част от изложения материал (особено глава 11) е базиран на лекционни курсове, полезни книги и др., които читателят може да си набави от интернет. Ето защо в цитираната литература са посочени линкове към тях. Освен това, в края на учебника, авторът е посочил, някои интересни сайтове, свързани с изчислителната химия и не само. От тях интересуващите се ще могат да научат много полезни неща за квантовохимичния софтуер, визуализиращите програми и др. Доста от софтуера е свободен и може да бъде инсталиран на подходящ компютър за ползване.

Авторът не претендира за изчерпателност на материала и би бил благодарен за забелязани грешки и препоръки.

Авторът изказва своята най-сърдечна благодарност на Гинка Делчева за внимателния прочит и корекция на ръкописа, както и на колегите от кат. Физикохимия на ПУ за моралната подкрепа при списването и издаването на настоящия учебник.

**3. Е-лекционен курс по Физикохимия I част, спец. Химия, РО**

<http://web.uni-plovdiv.bg/vdelchev/physchem/>

Учебни → Физикохимия → 1. Лекции по Физикохимия I част, Химия, РО (доц. В. Делчев)
(парола за отваряне на архивите: *питай автора!*)

Курсът включва лекции по темите: 1) Химична термодинамика. Основни понятия- система, термодинамични параметри, термодинамично състояние. Уравнение на състоянието. Уравнение на състоянието на идеален газ; 2) Нулев принцип на термодинамиката. Построяване на температурната скала; 3) Първи термодинамичен принцип. Енергия- закон за еквивалентното превръщане на енергията. Топлина и работа. Вътрешна енергия; 4) Термодинамика на идеален газ. Топлинни капацитети. Температурна зависимост на топлинните капацитети. Енталпия. Уравнение на адиабатата на идеален газ; 5) Термохимия. Топлинни ефекти на химичните реакции при $V=\text{const}$ и при $p=\text{const}$. Закон на Хес. Топлини на изгаряне, образуване, разтваряне; 6) Температурна зависимост на топлинните ефекти. Закон на Кирхоф; 7) Недостатъчност на първи термодинамичен принцип за описание на природните процеси. Видове процеси. Формулиране на втория термодинамичен принцип. Кръгов процес на Карно; 8) Ентропия. Определяне посоката на процеса в адиабатно изолирана система. Изчисляване изменението на ентропията; 9) Статистическо тълкуване на ентропията. Граници на приложение на втория термодинамичен принцип; 10) Неприложимост на ентропията при установяване посоката на химичните процеси. Енергия на Хелмхолц. Енергия на Гибс; 11) Уравнение на Гибс-Хелмхолц. Термодинамични потенциали. Характеристични функции; 12) Химичен потенциал- въвеждане, дефиниране, физичен смисъл. Връзка на химичния потенциал с концентрацията; 13) Термодинамика на реален газ. Отклонение на реалния газ от състоянието на идеалния. Уравнение на Ван-дер Ваалс. Летливост (фугативност); 14) Топлинна теорема на Нернст. Следствия. Постулат на Планк. Приложение на разширената топлинна теорема; 15) Химично равновесие. Степен на извършване на реакцията. Термодинамичен извод на закона за действие на масите. Химично равновесие в хетерогенна система; 16) Влияние на температурата и налягането върху равновесната константа. Уравнение на реакционната изобара (изохора) на Вант Хоф; 17) Изобарен потенциал на химична реакция. Уравнение на реакционната изотерма на Вант Хоф-значение. Стандартен изобарен потенциал- методи за неговото изчисляване. Посока на химичните процеси; 18) Термодинамика на фазовите превръщания от I и II род. Ентропия на изпарението; 19) Фазови равновесия. Основни понятия. Основен закон на фазовите равновесия – закон на Гибс. Приложение; 20) Разтвори. Обща характеристика на разтворите. Парциални молни величини. Уравнение на Гибс- Дюхем. Равновесие течен разтвор- наситени пари. Закон на Раул; 21) Реални разтвори. Положителни и отрицателни отклонения от закона на Раул. Безкрайно разредени разтвори. Закон на Хенри. Регулярни и атермални разтвори; 22) Колигативни свойства на разтворите. Температура на кипене и замръзване на разтвори на нелетливи вещества. Ебулиоскопия и криоскопия. Осмотично налягане; 23) Активност. Коефициент на активност. Методи за определяне. Закон за разпределението; 24) Равновесие на течни разтвори с газове. Закон на Хенри. Зависимост на разтворимостта от температурата; 25) Равновесие на течност с пара. Закони на Гибс- Коновалов; 26) Равновесие на кристал с течен разтвор в бинерна система.

Забележка! Лекциите по Физикохимия II за спец. Химия, РО са също в процес на товарене на страницата на кат. Физикохимия.

Е-семинари по Физикохимия I част, спец. Медицинска химия, РО

<http://web.uni-plovdiv.bg/vdelchev/physchem/>

Учебни → Физикохимия → 1.Семинарни упражнения по Физикохимия I част, Медицинска химия, РО (доц. В. Делчев)
(парола за отваряне на архивите: *питай автора!*)



4. Е-лекции по Квантовохимично моделиране спец. Компютърна химия - магистри, 30

**<http://web.uni-plovdiv.bg/vdelchev/physchem/>
Учебни → Квантовохимично моделиране**



САМООЦЕНКА НА ПРИНОСИТЕ

Научна работа

Кандидатът има принос към фундаменталните научни изследвания на механизми на химични реакции. Основните приноси на изследванията могат да се групират в три направления, а именно: 1) изследване на структури и реакции в основно състояние; 2) изследване на структури и реакции във възбудено електронно състояние; и 3) термодинамично изследване на фазови равновесия.

1) Изследване на структури и реакции в основно състояние

Основните приноси са свързани с изясняване на електронната и геометричната структура на β -дикарбонилите малоналдеhid (статия № 3), ацетилацетон (статии № 7,35), някои 3-оксопропионил халогениди (статия № 16), β -цистеаминилмалоновата киселина (статия № 23) и механизмите на кето-енолна тавтомерия в газова фаза. Намерени са преходните състояния на реакциите като седлови точки от първи род, както и тези, свързани с ротационните превръщания на плоските енолни форми на ацетилацетона (статия № 19). При ацетилацетона е изяснена ролята на дифузните функции за изчисляване на енергиите на съединенията и термодинамичните функции на кето-енолните превръщания (статия № 35).

Изследванията имат принос също към изясняване на механизмите на реакциите на вътрешномолекулен протонен пренос в биоорганични ароматни съединения като барбитуровата киселина (статия № 14), аденина (статия № 22), урацила (статии № 32,45), цитозина (статия № 39) и тимина (статия № 66). Намерени са преходните състояния на реакциите и са установени енергетичните бариери на тавтомерните превръщания. Изследвани са водородно свързаните комплекси на голяма част от тези съединения с вода (статии № 29,40,41,42,60,66) и други протни молекули като метанол (статии № 26,29,37,40,41,42) и млечна киселина (статия № 33). Оценена е стабилността на комплексите по енергиите на свързване (изчислени с орбитали "духове"). Изследванията показват, че реакциите на междумолекулен протонен пренос протичат през едно преходно състояние и ниски енергетични бариери в сравнение с реакциите на вътрешномолекулен протонен пренос.

Механизмът на ацилиране на оксалоцетната киселина с ацетилцистеамин (крайният фрагмент на ацетил-CoA) е изяснен с помощта на DFT изчисления (статия № 36). Установено е, че най-вероятният механизъм е този, който протича през енолната форма на оксалоцетната киселина.

Кандидатът е участвал, съвместно с група от ТУ-Виена, в изследвания за изясняване на структурата на NXO-модифициран пептид (статия № 69) чрез сравняване на експерименталните с теоретичните (B3LYP) ^1H NMR спектри на различни изомери на пептида в разтворител.

С помощта на HF пресмятания е изяснена структурата на комплекса на Fe^{2+} с 4-нитрокатехол и 2,3,5-трифенил-2Н-тетразол (статия № 73). Установено е, че най-стабилната конфигурация е на нискоспиновия тетраедричен комплекс. На същото теоретично ниво са изследвани структурите на [3,3'-(3,3'-диметокси-4,4'-бифенилен)бис[2,5-ди(4-нитрофенил)-2Н-тетразолиев] хлорид и неотетразолиев хлорид (неутрални



съединения и катиони) с цел установяване на най-изгодните конфигурации при комплексообразуване с Fe^{3+} (статия № 69).

2) Изследване на структури и реакции във възбудено електронно състояние

Това е ново направление, което започва след специализацията на кандидата в групата на проф. В. Домке (ТУ – Мюнхен, 2008-2009 г.) – водещ световен учен в теоретичното изследване на механизмите на фотореакции на органични съединения. Съгласно обектите на изследване основните приноси са:

➤ *изясняване на механизми на фотореакции в β -дикарбонили.* Предложен е механизъм на фотоциклодимеризация на енолната форма на малоналдехида по реакционен път на $^1\pi\pi^*$ възбуденото състояние до *транс-анти* циклобутанов димер (статия № 49). Намерено е конично сечение S_1/S_0 на реакцията, което обяснява този процес (статия № 51).

Установен е механизъмът, по реакционния път на $^1\pi\pi^*$ възбуденото състояние, на фоторазкъсване на вътрешномолекулната водородна връзка в енолната форма на ацетилацетона чрез ротация около C=C връзката (статии № 44, 52). По този начин е обяснен експерименталният факт (J. Phys. Chem. A, 2001, 105, 10832), който показва, че при облъчване на ацетилацетона с UV светлина се генерират други плоски енолни конформери (без H-връзка) на съединението.

Беше установено, че при включване на енолната форма на ацетилацетона в β -циклодекстринов пръстен се затруднява протонния пренос между двата кислородни атома, както в основно така и във възбудено състояние (статия № 64).

➤ *изясняване на механизми на фотореакции с пиримидинови производни.* Изследвани и предложени са механизми на безизлъчвателна дезактивация на голям брой пиримидинови производни: урацил (статия № 47), 4-пиримидинон (статия № 47), (тио)барбитурова киселина (статии № 54, 56, 58, 67, 68,), (изо)цитозин (статии № 50, 55, 57, 59, 76), 2,4-диаминопиримидин (статия № 76); които обясняват високата фотостабилност на пиримидиновите нуклеобазы и фототавтомерията на техни близки аналози / производни. Доказано е, че фототавтомерията протича по реакционните пътища на $^1\pi\sigma^*$ възбудените състояния, а вътрешната конверсия на пиримидиновите нуклеобазы до стабилните си тавтомерни форми, в подкрепа на тяхната фотостабилност, протича по реакционните пътища на $^1\pi\pi^*$ възбудените състояния.

Предложени са механизми на фотоциклодимеризация на две молекули урацил до *цис-син* циклобутанови димери (статии № 46, 65) и оксетанов димер (статия № 65). Доказано е, че фотопроцесите протичат по реакционните пътища на $^1\pi\pi^*$ възбудените състояния.

➤ *изясняване на механизми на фотореакции с пуринови производни.* Локализирани са няколко конични сечения S_1/S_0 на оксо, хидрокси, N9H и N7H тавтомерите на гуанина (статии № 62, 63) и са предложени реакционни пътища на $^1\pi\pi^*$ възбудените състояния, които достигат до тях (статия № 65). Предложен е най-изгоден, безбарьерен, реакционен път, по който се обяснява фотостабилността на тази пуринова нуклеобаза.

За ксантина и хипоксантина са локализирани две конични сечения S_1/S_0 , които биха обяснили вътрешната конверсия на $^1\pi\pi^*$ възбудените състояния до основно състояние (статия № 70).

➤ *изясняване на фотостабилността и механизмите на фотореакции в други ароматни съединения.* Установена е връзка между водородно



свързаната вода и вертикалните енергии на възбуждане в няколко водородно свързани комплекса на серотонина с вода (статия № 61).

Предложени са механизми на протонен пренос в 3,5-динитрокатехол във възбудено електронно състояние (статия № 71). Установени са структурата и стабилността на комплексите на V^{5+} и W^{6+} и динитрокатехола (статия № 71).

Механизмите на вътрешна конверсия на възбудените състояния до основно състояние в два позиционни изомера на хидрокси-метил-пиридина са установени (статия № 74). Локализирани са конични сечения S_1/S_0 , които обезпечават тези фотофизични процеси.

➤ *изясняване на експериментални данни от MATI (mass-analyzed threshold ionization) и мас-селективна УВ спектроскопия. С помощта на ab initio изчисления са установени три стабилни конформера-катиона на 2-фенилетанола, които са регистрирани с MATI спектроскопия (статия № 43).*

Структурата на четири конформера на псевдоефедрина е намерена за основно и за първото възбудено електронно състояние. Изчислени са адиабатните енергии на възбуждане и моментите на преходите, които помогнаха за отнасяне на някои експериментални вибрационни ивици на псевдоефедрина (статия № 53).

3) Термодинамично изследване на фазови равновесия

Експериментално са изследвани (при стайна температура и стандартно налягане) три трикомпонентни системи конструирани от компонентите ацетилацетон, вода и алкохолите метанол/етанол/изо-пропанол (статия № 17). Най-голяма хетерогенна област ($s = k - f = 3 - 2 = 1$) е установена за трикомпонентната система ацетилацетон-вода-метанол.

Учебна работа

Разработени са лекционни курсове по: Квантова химия (хорариум 30 часа лекции), Квантовохимични методи (хорариум 45 часа лекции), Физикохимия I част (хорариум 45 часа лекции) и Физикохимия II част (хорариум 45 часа лекции). По първите два лекционни курса кандидатът е издал свои учебни помагала. Кандидатът е публикувал на страницата на кат. Физикохимия* своите лекции по Физикохимия I.

Кандидатът участва активно в разработване на лабораторни упражнения по физикохимия в катедрата. Предстои издаване на ръководство с лабораторни упражнения, в което кандидатът е съавтор. Разработил е упражнения за измерване на осмотичното налягане на захарен разтвор, определяне на интегралните топлини на разтваряне на кристални вещества, измерване на вискозитета на вискозни течности и др. Участва активно в модифицирането на старите лабораторни упражнения.

Кандидатът е разработил цикъл упражнения за дисциплините Квантовохимични методи (бакалаври) и Квантовохимично моделиране (магистри), които може да бъдат намерени на страницата на кат. Физикохимия. Кандидатът е съавтор в ръководство за лабораторни упражнения по "Приложна физикохимия" (за магистри), в което той участва с упражнения за програмите MOPAC и GAMESS-US.

* <http://web.uni-plovdiv.bg/vdelchev/physchem/>