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Scientific biography of Professor DSc Tsonko Mitev Kolev

Tsonko Mitev Kolev was born on 10 January 1948 in Gradnitsa, district Gabrovo. In 1973 he completed his Master's degree in Organic synthesis and Chemistry of natural pharmaceutical drugs at the Faculty of Chemistry, Sofia University.

In 1975 Tsonko Kolev began to work as Junior scientist in the Laboratory for Structural Organic Chemistry at the Institute of Organic Chemistry, Bulgarian Academy of Sciences under scientific supervision of Prof. Ivan Juchnovski in the field of electronic structure of conjugated organic compounds and the genetically related negative ions, which are intermediates in important organic reactions, by means of the combined application of infrared spectroscopy, quantum chemical methods, the correlation analysis and isotope labelled compounds. They work on the transmission of polar effects of substituents through the systems of conjugated bonds on the characteristic frequencies and intensities, and particularly the exponential decrease of the polar effect of the substituents with the increase of the number of the double bonds in the polyene system. Tsonko Kolev defended his PhD thesis devoted to IR spectral investigation of anion radicals of aromatic ketones in 1982. The infrared spectra of anion-radicals of aromatic ketones (ketyls) were interpreted correctly for the first time by means of isotopic labelled compounds, which led to the correction of a number of errors in band assignment and some corresponding findings concerning the influence of the structure over infrared spectra of these anion-radicals. It was shown that infrared spectroscopy could give information about the form of the orbital of the unpaired electron, as well as about the presence of separate weak interactions between molecular fragments due to the peculiar symmetry of this orbital.

In 1987 Tsonko Kolev has been awarded the Alexander von Humboldt Research Fellowship for Postdoctoral Researchers. He joined the research group of Prof. Dr. Paul Bleckmann at the Faculty of Chemistry, Structural Chemistry Department, University of Dortmund (1987–1988 and 1991–1992).

Tsonko Kolev acquired the academic rank Associate Professor at the Institute of Organic Chemistry, Bulgarian Academy of Sciences in 1992. He organized a working group handling with organic materials for nonlinear optics. In 2001 he defended his Doctor of Sciences degree – dissertation titled "Vibrational and structural analyses of some aromatic, aryl aliphatic ketones, diketones and their derivatives – potential materials for nonlinear optics".

He became Full Professor in Organic Chemistry in 2005.

In the period 2005–2013 Prof. Kolev was Head of the Department of Organic Chemistry at Plovdiv University and Member of the Faculty Council.

Scientific research field

Tsonko Kolev's scientific research fields cover: design, synthesis, spectral and structural elucidation of novel organic materials with large nonlinearoptical (NLO) and electrooptical (EO) coefficients and good photochemical resistance against laser beam.

The following methods were used: spectral ones (IR, Raman, UV-vis and Fluorescent spectroscopy), single crystal X-ray analysis and quantum chemical calculations of hydrogensquarates, squarates and esteramides of squaric acid with amino acids and aminoacid amides.

Another important field of investigation is the synthesis, spectral and structural elucidation of pyridinio betaines of squaric acid. Quantum chemical calculations were performed to obtain electronic structure and vibrational data, using DFT and *ab initio* methods.

In the last years the efforts of Prof. Kolev are directed to the synthesis, spectral and structural elucidation of new stilbazolium salt with enlarged π-conjugated system and their functional thin films deposited by pulsed laser deposition (PLD) using UV TEA N_2 laser onto glass substrates and KCl, NaCl single crystals.

Last but not least, Prof. Kolev works on the complete elucidation of new dicyanoisophorone deriva-

tives – nonlinear optical and electrooptical materials with possibility to tune their mechanical and electrical properties.

Lecturer activities

In the period 2004–2013 Prof. Kolev worked at the Faculty of Chemistry at the University of Plovdiv giving lectures on Organic Chemistry for the Bachelor students. He also gave lectures on Medicinal chemistry, Organic Chemistry, Organic Synthesis and X-ray analysis for the Master degree.

Between 2006 and 2010 he gave lectures at Sofia University on Modern methods of Organic Structural Analysis, Infrared and Raman Spectroscopy and New NLO materials (Master degree).

Since 2014 Prof. Kolev is lecturer at the South West University in Blagoevgrad, course Instrumental methods in Organic Chemistry for the Master students.

Scientific Supervisor

Since 2000 Prof. Kolev is Scientific Supervisor of 9 PhD students: Zornitza Glavcheva, Denitsa Yancheva, Mariana Topuzova, Rumyana Bakalska, Plamen Angelov, Emilia Cherneva, Tsanko Tsanev, Mina Todorova and Daniela Petrova.

Scientific projects

Manager and lecturer at the International Summer School on Applied Spectroscopy and X-Ray Analysis for young scientists and PhD students from Bulgaria, Poland, Czech Republic, Serbia, Macedonia, Slovenia, Croatia, Albania, Turkey, Hungary and Romania held every summer between 2004 and 2009 in the Institute of Organic Chemistry, Bulgarian Academy of Sciences supported by Deutscher Akademischer Austauschdienst (DAAD).

Scientific projects BUL 001 96 (1996–1998) and BUL 006 99 (1999–2001) between the Institute of Organic Chemistry, Bulgarian Academy of Sciences, and Bundesministerium für Bildung und Forschung.

Scientific projects between the Institute of Organic Chemistry, Bulgarian Academy of Sciences, and Deutscher Akademischer Austauschdienst (DAAD) 2002–2004 and 2005–2007.

"Sandwich program" with PhD student Zornitza Glavcheva at the University of Dortmund, supported by Alexander von Humboldt Stiftung (2001).

Award "Institutspartnerschaft" (2003–2004) with Prof. Rüdiger Wortmann (Technical University Kaiserslautern) and Prof. Kolev (Institute of Organic Chemistry, Bulgarian Academy of Sciences) supported by Alexander von Humboldt Stiftung. As a result of this project series of nonlinear optical chromophores containing a cyclobutenedione fragment as electron-acceptor group have been synthesized and investigated and their linear and nonlinear optical properties were proven by electro-optical absorption measurements in solution. The negative values of the static hyperpolarizabilities of the NLOphores studied, associated with dipolar ground-state structures, increase significantly on going from donor to acceptor substituent.

Prof. Kolev was Invited Professor at the University of Dortmund (1994).

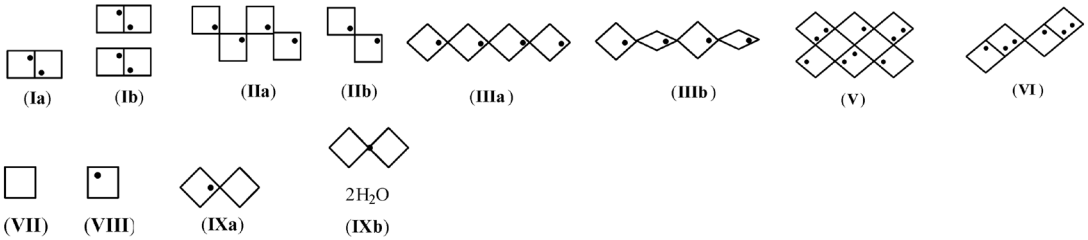
For the "Sandwich" program at the University of Dortmund supported by Deutscher Akademischer Austauschdienst (DAAD) Prof. Kolev chose PhD student Tsanko Tsanev (2008).

In the period 2009–2010 Prof. Kolev was co-principal investigator of a German-Bulgarian Research Project supported by the German Research Society (DFG) grant SP 255/21-1 dedicated to NLO and EO properties of organic materials at Technical University of Dortmund, Germany.

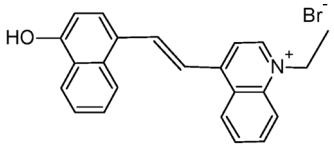
Scientific contributions

The basic and most essential scientific contributions of Prof. Kolev, consist in both experimental and theoretical studies on the field of design, synthesis, spectral and structural elucidation of novel organic materials with large nonlinearoptical (NLO) and electrooptical (EO) coefficients and good photochemical resistance against laser beam. The spectral (IR, Raman, UV-vis and Fluorescent spectroscopy) and single crystal X-ray analysis and quantum chemical calculations of hydrogensquarates, squarates and esteramides of squaric acid with amino acids and amino acid amides. As a results 8 new structural motifs of hydrogensquarates are established: Ib, IIb, IIIb, 4b, 4c, VIII, IXa, IXb.

The synthesis, spectral and structural elucidation of series pyridinio betaines of squaric acid are performed. Quantum chemical calculations are made to obtain electronic structure and vibrational data, using DFT and *ab initio* methods. In the last years the efforts of prof. Kolev are directed to the synthesis, spectral and structural elucidation of new stibazolium salts with enlarged π-conjugated system and their functional thin films deposited by pulsed

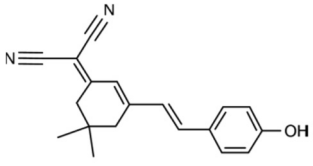


laser deposition (PLD) using UV TEA N_2 laser onto glass substrates and KCl, NaCl single crystals. The effective $\chi^{(2)}$ values are determined to be 1.40 and 0.95 pm/V for p and s polarization, respectively, so the $\chi^{(2)}$ in the p polarization case is enhanced by about 45%, with respect to the s case. The chemical diagram of (E)-1-Ethyl-4-(2-(4-hydroxynaphthalen-1-yl)vinyl)quinolinium Bromide is shown below:



The determined effective $\chi^{(3)}$ value was found to be 6.5×10^{-20} m^2 V^{-2} one of the best values measured for organic compounds. These results were published in the Journal of Physical Chemistry C (2012), 116, 7144−7152.

The complete elucidation of series of new dicyanoisophorone derivatives – nonlinear optical and electro optical materials with possibility to tune of their optical and mechanical properties. As a result of this investigation it was found second-order optical properties of anionic 3-dicyanomethylen-5,5-dimethyle-1-[2-(4-hydroxyphenyl)ethenyl)]-cyclohexene (1) with crystalline sizes from 10 nm to 300 nm were studied. An electric field enhancement of effective second-order susceptibility at 1064 nm for the crystallites incorporated into the oligoetheracrylate photopolymer matrices from 3.1 pm/V to 7.8 pm/V was discovered corresponding to hyperpolarizability increase from $0.12.10^{-30}$ esu to $0.21.10^{-30}$ esu. The evaluated intrinsic hyperpolarizability achieves value about 0.037, which is comparable with the best organic molecule. Further investigations of Prof. Kolev and researchers from France, Germany and Poland were on physics of the NLO materials on the basis of compounds with the quinoide like structure.



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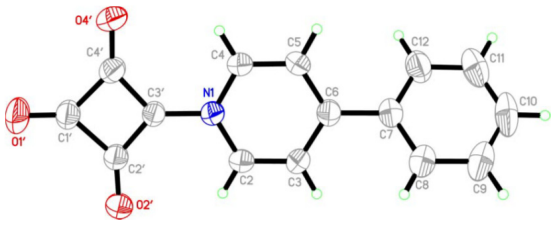
The novel composites based on the 1-methyl-4-[2-(3-methoxy-4-oxocyclohexadienyliden) ethyliden]-1,4-dihydropyridine (I) chromophore incorporated into the polymer PMMA matrices in 7.5% weight content deposited on mica substrate They have found that the SHG at 1,064 nm was increased saturating after 4–5 min. of the dc-treatment. The main alignment process was observed during first 2 min of the dc-field poling. Afterwards, the process was saturated achieving the maximal values after about 8 min. It was crucial that more flexible for alignment was temperature of about 350 K. They have measured values of second order optical effect of about122 pm/V at 1,064 nm fundamental laser wavelength. This effect show very weak reversibility after the dc-field switching off.

The linear and nonlinear optical properties of different substituted piridinio betaines of squaric acid were established by electro-optical absorption measurements (EOAM) in dioxane solution. It was found all chromophores studied exhibit intense absorption bands in the visible region within 372–441 nm, accompanied with decrease in dipole moment upon excitation.



The static hyperpolarizabilities of the NLO-phores studied depend strongly on the substituent in the pyridinium ring and increase significantly going from donor to acceptor substituent. Specifically, the noncentrosymmetrically crystallizing 4-benzoyl compound showed the highest static hyperpolarizability β_0 –26.19.

Prof. Kolev published 225 research papers, 2 books, 4 chapters of books and an invited review.

The books and chapter of books are listed below:

1. Kolev, T. (2007) *Quantum chemical, spectroscopic and structural study of hydrochlorides, hydrogensquarates and ester amides of squaric acid of amino acid amides, Chapter of book "Progress in Quantum Chemistry Research" E. Hoffman (Ed),*

Nova Science Publishers, Inc., Hauppauge, NY 11788, USA, ISBN: 1-60021-621-8.

2. Kolev, T. (2008) *Quantum Chemical, Spectroscopic and Structural Study of Hydrochlorides, Hydrogens Squarates and Ester Amides of Squaric Acid, Book – 95 pages Nova Science Publishers, Inc., Hauppauge, NY 11788, USA, ISBN: 978-1-60456-431-0.*

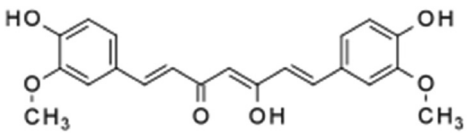
3. Koleva, B., Kolev, T. M., Spiteller, M. (2011) Book chapter: *"Spectroscopic Analysis and Structural Elucidation of Small Peptides", in "Advances in Chemistry Research vol. 3, pages 675–755 J. C. Taylor (Ed.), Nova Science Publishers, Inc., Hauppauge, NY, 11788, USA.*

4. Ivanova, B., Kolev, T. (2011) *Linearly Polarized IR Spectroscopy Theory and Applications for Structural Analysis--Book. Taylor and Francis Group, CRC Press, Boca Raton, USA ISBN: 978-1-4398-2559-4.*

5. Kolev, T., Spiteller, M., Koleva, B. (2010) *Spectroscopic and structural elucidation of amino acid derivatives and small peptides – experimental and theoretical tools, Amino Acids, Review, 38, 45-50.*

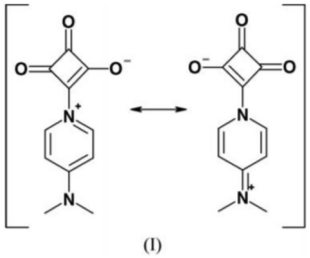
6. Tsonko Kolev, Rumyana Bakalska, Mina Todorova (2016) *Efficient π electrons delocalization in two styrylquinolinium dyes – organic materials for second order nonlinear application Chapter of book "BULGARIAN-GERMAN SCIENTIFIC COOPERATION: PAST, PRESENT, AND FUTURE" PROCEEDINGS OF THE HUMBOLDT-KOLLEG Sofia, November 26–28, 2015, Faber Publishing House, 2016 pp. 209–221, ISBN 978-619-00-0517-9.*

The citations for the period 1990–2018 are 2426 in total (Scopus) and 2845 (Google). The most cited article is: Kolev, T., Velcheva, E., Stamboliyska, B., Spiteller, M. (2005) DFT and Experimental Studies of the Structure and Vibrational Spectra of Curcumin, International Journal of Quantum Chemistry, 102, 1069–1079 – 255 citations until July 2018.



In this work Prof. Kolev has unambiguously shown by vibrational spectroscopy and DFT calculations that the compound possesses outstanding antioxidant activity due to enol form which keeps the molecule conjugated.

Article in journal with highest impact factor: Kolev, T., Yancheva, D., Stoyanov, St. (2004) Synthesis, Spectral and Structural Elucidation of Some Pyridinium Betaines of Squaric Acid – Potential Materials for Nonlinear Optical Applications, Advanced Functional Materials, 14, 799 –804 – IF 10.48. An example of 4-dimethylamino pyridinio-betaine of squaric acid is presented on the following figure:



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Scientific Awards

In 2010 Prof. Kolev received the Award of Plovdiv University for the best scientist on the field of Natural Sciences.

In 2011 he received the National Pitagor Award (Pythagoras) of the Ministry of Education and Sciences for the best scientist on the field of Natural Sciences.

In 2012 Prof. Kolev is nominated for corresponding member of Bulgarian Academy of Sciences by Plovdiv University for his achievements in the field of physical organic chemistry and organic material science.

He was awarded Alumni Program of Alexander von Humboldt Foundation (2013–2015) with host Prof. Dr. Dr. h. c. Michael Spiteller, Institute of Environmental Research at the Technical University (TU) Dortmund.

Family life

Prof. Kolev has two daughters – Martina and Tsonka. Together with granddaughter Sophia they love spending time together in Gradnitsa village – the birth place of Prof. Kolev, at the foot of the Central Balkan Mountains.

Acknowledgements

Prof. Kolev has been collaborating with many scientists from Bulgaria and abroad. The research has been supported by many German and Bulgarian organizations. They are listed below:

- Alexander von Humboldt Stiftung

Prof. Kolev would like to express his sincere gratitude to the Alexander von Humboldt Foundation for the continuous support of his research. The research fellowships provided him with the unique opportunity to work with prominent scientists at recognized educational and research institutions such as the Technical University of Dortmund, Department of Organic and Structural Chemistry (Prof. Paul Bleckmann (1988–1989 and 1991–1992), Technical University Kaiserslautern (Prof. Dr. Rüdiger Wortmann 2003–2004). The donation of Bruker Smart Diffractometer X2S made possible the solution of many structures included in his publications. He also wants to thank for Renewed Research Sponsorship 2013–2015.

- Deutsche Luft und Raumfahrt (DLR, Osteuropa-Verbindungsbüro)
- Bundesministerium für Bildung und Forschung (BMBF)
- Deutscher Akademischer Austauschdienst (DAAD)
- Deutsche Forschungsgemeinschaft
- National Science Fund of Bulgaria

Tsonko Kolev wants to thank following colleagues for their collaboration, exchange of ideas and fruitful discussions during the preparation of the manuscripts:

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- Prof. Dr. Michael Spiteller – Technical University Dortmund, Germany
- Prof. Dr. Hans Preut – Technical University Dortmund, Germany
- Prof. Dr. Iwan Kityk – Technical University Czestochowa, Poland
- Prof. Dr. Bouchta Sahraoui – University of Angers, France
- Dr. Rüdiger Seidel – Ruhr University Bochum, Germany
- Prof. Dr. Rositsa Petrova – Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences
- Prof. Dr. Boris Shivachev – Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences
- Assoc. Prof. Dr. Stefan Kotov – University Assen Zlatarov, Bourgas
- Assoc. Prof. Dr. Zornitza Glavcheva – Tohoku University, Sendai, Japan
- Assoc. Prof. Dr. Bistra Stamboliyska – Institute of Organic Chemistry, Bulgarian Academy of Sciences
- Assoc. Prof. Dr. Evelina Velcheva – Institute of Organic Chemistry, Bulgarian Academy of Sciences
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- Assoc. Prof. Dr. Rumyana Bakalska – University of Plovdiv "Paisii Hilendarski"
- Dr. Mina Todorova – University of Plovdiv "Paisii Hilendarski"
- Dr. Sonya Zareva – Sofia University "St. Kliment Ohridski"
- Dr. Tsanko Tsanev – Bourgas University "Assen Zlatarov", Bourgas
- Dr. Daniela Petrova – Military Medical Academy, Sofia
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