



Professor Zbigniew Ryszard Grabowski holds a very special place in science. In the photochemical community, his name is inseparable from the term he coined three decades ago: *TICT*. After years of thorough, often emotional discussions, the concept of *Twisted Intramolecular Charge Transfer* excited states seems to be well established. Researchers often (perhaps too often!) evoke conformational changes in photoexcited flexible electron donor-acceptor systems to interpret the complex behaviour (dual fluorescence in particular) of their molecules.

Starting his carrier already as a student, at the Chemistry Department of the Warsaw University, Z.R. Grabowski did research on electrode kinetics and on stereochemistry of electrode processes. He discovered the effects of electric field strength on electrode reactions mechanisms.

Founder of the Photochemistry and Spectroscopy Laboratory in the Institute of Physical Chemistry of the Polish Academy of Sciences, he contributed to the development (in cooperation with Jan Jasny and Józef Koszewski) of unique spectral instruments for absorption and luminescence measurements.

In the field of excited state acid-base equilibria, his name is associated with the so-called generalized Förster cycle, the idea he promoted together with wife Anna.

Yet another area of his passions and scientific activities includes the chemical evolution and origins of life, subjects related to astrochemistry.

We were given a chance to do our PhDs, to work, and to mature in the laboratory of Professor Grabowski. Not only did he teach us that science should be done with no compromise, but also that scientists' duties extend beyond pure research. Actively involved in matters crucial for the society, he is having the courage to speak out boldly against any injustice – setting examples that are not always easy to follow.

This special issue of the *Polish Journal of Chemistry* contains contributions from students, associates, and friends of Professor Grabowski. We all want to congratulate him on his birthday. Many happy returns, Zbyszku!

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Quantum Chemical Study of Hydroxylation of Alkanes by Hypofluorous Acid

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The experimentally observed hydroxylation of alkanes by hypofluorous acid (one of Rozen's oxidation reactions) was investigated using the methods of quantum chemistry. It was shown that the high efficiency of the reaction may be explained by self-catalysis. The oxidizing HOF molecule transfers the oxygen atom to a substrate, which is accompanied by the HF formation, while the second hypofluorous acid molecule stabilizes the oxidizing HOF molecule by a hydrogen bond. The hydroxylation barriers were found to decrease with increased coordination of the oxidized carbon atom by methyl groups, in agreement with the experiment. In the gas phase, the calculated DFT/B3LYP reaction barriers amount to 22.5, 14.5, 9.0, and 6.4 kcal/mol for oxidation of methane, ethane, central carbon atoms of propane, and 2-methylpropane, respectively; for a terminal C–H propane bond, a barrier was enumerated to 13.9 kcal/mol. It was also found that the reaction can be catalyzed by the product molecule, hydrogen fluoride (as first suggested for ethylene in Sertchook R., Boese A.D., Martin J.M.L., *J. Phys. Chem. A*, **110**, 8275 (2006)), and common features of the H-bond assisted catalysis were investigated. The analogous but very much less favorable hydroxylation by hypochlorous acid molecule was also briefly discussed.

Key words: alkane hydroxylation, Rozen's reaction, hypofluorous acid, catalysis

Scaled Molecular Dynamics Simulations for Ultraintense Laser – Cluster Interactions

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New developments in the field of charge separation in large finite systems pertain to extreme ionization of elemental and molecular clusters in ultraintense laser fields (peak intensities 10^{15} – 10^{21} Wcm⁻²) with the production of highly charged ions (*e.g.*, completely ionized deuterium, water and methane clusters or Xe³⁶⁺). Concurrently and parallel to extreme ionization, Coulomb explosion occurs with the production of high-energy (keV–MeV) ions. The large cluster and nanodroplet sizes, for which Coulomb explosion drives efficient table-top dd fusion and nucleosynthesis with heavier nuclei, preclude the use of the traditional particle molecular dynamics simulation methods. We consider a scaling method for molecular dynamics and explore its validity conditions. The scaling method will be applicable for large finite systems (with a number of constituents up to 10^8 and sizes up to 100 nm) where particle motion is governed by long-range (*e.g.*, Coulomb) interactions.

Key words: cluster extreme ionization, Coulomb explosion, table-top nucleosynthesis, numerical methods

On the Nature of the Interaction in Ternary Water-Sulfur Dioxide Complexes

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The interpretation of the intermolecular interaction energy in the ternary 2:1 and 1:2 trimers has been done. The decomposition of the total interaction energy using two- and three-body symmetry-adapted perturbation theory (SAPT) providing physically meaningful components: electrostatic, induction, dispersion and exchange terms was applied. Four $(\text{H}_2\text{O})_2 \cdots \text{SO}_2$ and two $\text{H}_2\text{O} \cdots (\text{SO}_2)_2$ trimers were analyzed. We compared the contribution of the sandwich-type pair with the contribution of the hydrogen-bonded pairs to the total interaction energy of the trimer. The assumption of pairwise additivity of the interaction in the ternary mixed trimers is not correct. The three-body nonadditivity terms represent as large as *ca.* 18% of the total interaction energy.

Key words: *ab initio*, SAPT, nonadditivity, sulfur dioxide-water interaction

Size-dependent Fluorescence Spectra of Individual Perylene Nanocrystals Studied by Far-Field Fluorescence Microspectroscopy Coupled with Atomic Force Microscope Observation

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Single particle fluorescence spectroscopy coupled with AFM observation is reported for perylene nanocrystals. Fluorescence spectral measurement for individual nanocrystals with the size from 100 nm to 500 nm and fluorescence anisotropy analysis demonstrate that the size dependence in fluorescence is in the intrinsic nature of nanometer-sized crystal of perylene. Single nanoparticle fluorescence shows the enhanced monomer (M-) emission compared to the bulk crystal and a blue-shift of excimer (E-) emission peak wavelength by decreasing the nanoparticle size. It is found for the first time that the size dependence is correlated well to the surface-to-volume ratio of nanocrystal. The size-dependent fluorescence is not attributed to a quantum confinement effect of exciton, but to a change in the elastic properties of nanocrystal with size, which in turn affects excimer formation. We discuss the decrease in elastic constant of crystal-line lattice due to large surface-to-volume ratio, and propose an empirical formula on the size-dependence of E-emission peak in the framework of the strong coupling model of exciton-phonon interaction.

Key words: organic nanocrystal, perylene, single particle spectroscopy, fluorescence spectroscopy, size dependence

Multi-Pulse Excitation Reveals a Novel Excited State Pathway in a Peryleneimide-Pentaphenylene Dyad

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The excited state properties of a peryleneimide-pentaphenylene dyad were investigated in detail using pump-probe, single photon timing and three-beam pulsed experiments. Upon excitation with 395 nm pulses ultrafast energy transfer was found to occur from the pentaphenylene to the perylene subunit. In polar solvents this excitation energy transfer is followed by charge transfer from the electron donor pentaphenylene to the electron acceptor perylene. A three-beam femtosecond transient absorption technique revealed the relaxation dynamics of a higher lying singlet state of the peryleneimide subunit to occur on a picoseconds time scale. These results demonstrate the potential use of the three-beam femtosecond technique in manipulating excited states processes.

Key words: perylenemonoimide, pentaphenylene, excited state, excitation transfer, charge transfer, femtosecond three-beam transient absorption

Carrier Dynamics and Optical Kerr Effect of Titanium Dioxide Single Crystals by Femtosecond Transient Grating Spectroscopy

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The photogenerated carrier dynamics and optical Kerr effect in rutile titanium dioxide (TiO₂) single crystals with (100), (110), and (001) faces were examined by femtosecond transient grating spectroscopy. The diffraction signal of the intensity grating in bare TiO₂ single crystal at 670 nm was considered to be due to free electrons or weakly trapped electrons nearby Ti⁴⁺ sites within the bulk. The decay curves of transient grating were strongly dependent on the excitation intensity but not on the types of crystal faces. The subsequent intensity-dependent relaxation was interpreted in terms of second-order electron-hole recombination kinetics with the rate constant of $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for both (110) and (100) faces. The optical Kerr dynamics of bare TiO₂ examined by resonant polarization grating and non-resonant intensity grating shows an ultrafast response similar to the system response function, indicating that the Kerr signal is mainly due to electronic polarization. By the excitation of conduction band electrons of reduced TiO₂ with the excess energy of 1.7 eV, the relaxation time constant of hot electrons within the conduction band was estimated to be 310 fs. In the long time region, the propagation of acoustic wave of 1.28 GHz was observed, which was due to the excess energy of hot electron converted into the thermal energy by electron-phonon scattering followed by the thermal relaxation.

Key words: titanium dioxide single crystal, transient grating, electron-hole recombination, optical Kerr effect, acoustic wave

Fluorescence Studies on Benzene and Benzene Aqueous Solution in Mesoporous Silica

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We have measured fluorescence spectra as well as fluorescence decay curves of highly ordered mesoporous silica, SBA-15 and FSM-16 including benzene or benzene aqueous solution as a function of temperature. An efficient energy transfer from benzene excited singlet state to a defect in the wall of mesoporous silica emitted at about 300 nm was found. On the basis of the decay analysis, it was suggested strongly that many of the benzene molecules exist in the proximity to the surface of pore wall owing to the strong molecular interactions between benzene and silica wall. It is noted that the defects in the silica wall seem to play an important role in understanding of the luminescence characteristics of chromophores embedded in mesopores.

Key words: mesoporous silica, energy transfer, defects in silica wall

Tentative Identification of C_3N^{\bullet} Radical Luminescence in Solid Krypton

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A product of cyanoacetylene photodissociation in Kr matrices gives rise to visible emission bands tentatively identified as due to the fluorescence and to the phosphorescence of the C_3N^{\bullet} radical. This assignment, which involves the low-lying $\tilde{A}^2\Pi$ state as the final one for both emissions, is based on the isotopic substitution study and on former theoretical predictions.

Key words: interstellar molecules, rare gas matrices, cyanoacetylene, fluorescence, phosphorescence, free radical

Influence of Rotational – Vibrational Coupling on Shape of Rovibrational Bands

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The integrated absorption coefficient of rovibrational bands is calculated for three different cases, namely for separated rotational and vibrational motions, for the non-rigid model which takes into account the coupling between above mentioned motions using the Kratzer-Fues potential and the soft body model, for which only rovibrational states exist. It is shown that the shape of *P* and *R* bands for higher rotational quantum numbers depends on the applied model of rotational – vibrational transitions.

Key words: intensity, IR-transitions, quantum dynamics

Real-Time Probing of Fast Photoinduced Charge-Transfer in Electron Donor-Acceptor Model Compounds and in Biological Photosensors

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We review some of our results on the role of solvent reorganization as an actual reaction coordinate in a few photoinduced charge-transfer processes concerning: dimethylaminobenzonitrile (DMABN), bianthryl and its 10-cyano-derivative and anthracene-dimethylaniline (ADMA), in solution at room temperature. These processes were studied by subpicosecond transient absorption spectroscopy. We also describe some of our recent results on charge-transfer processes involved in the primary response of photoactive proteins such as the photoactive yellow protein (PYP) and the oxyblepharismine-binding protein (OBIP). The deciding role of the protein environment in the photophysics of the chromophore is emphasized.

Key words: charge-transfer, internal twisting, ultrafast spectroscopy, biological photoreceptors

Conical Intersections and the Electronic Structure of the Excited States of N-Phenyl Pyrrole – a Prototype Molecule Exhibiting Dual Fluorescence

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The mechanism leading to dual fluorescence in substituted benzene derivatives is discussed using N-phenyl pyrrole (PP) as a test molecule. A model based on the quasi-Jahn-Teller distortion of the charge transfer (CT) state of PP, similar to that of the benzene anion radical, is presented. The model helps to locate stationary points on the S_1 singlet excited state potential surface, and to construct an energy level diagram. The energy and structure of the quasi Jahn-Teller degeneracy which is between S_3 and S_2 are computed, as well as those of three conical intersections connecting S_1 and S_2 . The findings indicate a complex nature of the S_1 state electronic state, containing several local minima, stationary points and surface crossings. The major structural change responsible for the stabilization of the CT state is the ring quinoid deformation which is a main component of the energy difference gradient vector in the branching space of all S_1/S_2 conical intersections. In the resulting charge transfer state (which is of quinoid structure) the pyrrole ring can either rotate to form a stabilized twisted species, or remain planar depending on substitution. This result holds also for DMABN and other molecules in which the donor is a substituted amine moiety. It is concluded, in line with a recent study on DMABN (Gomez *et al.*, *J. Amer. Chem. Soc.*, **127**, 7119 (2005)) that the TICT and PICT models are not mutually exclusive, but two different manifestations of the same physical reality.

Key words: dual fluorescence, conical intersections, phenyl-pyrrole, intramolecular charge transfer

Notes on the Fluorescence and the Nature of the Photocoloured Form in Photochromic Azomethines

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The analysis of the results obtained by recent investigations of photochromic azomethines (anils), including the author's data, shows that the pathway for the photocoloured product generation proceeds consecutively *via* (i) the S_1 excited state of the NH structure (S_1^{NHflu}), arising from the excited state intramolecular proton transfer $\text{OH} \rightarrow \text{NH}$ and responsible for the fluorescence with the anomalous Stokes shift (ASSflu); (ii) the ASSflu quenching TICT structure (S_1^* state) with the twisted "keto" ring ($\alpha = 90^\circ$) in the *trans* isomer (with respect to the C–N bond, $\beta = 0^\circ$); (iii) the unstable *trans* twisted post₁TICT structure ($\alpha = 90^\circ$, $\beta = 0^\circ$) in the S_0 state, which is the immediate precursor of (iv) low-stability post₂TICT *cis* structure twisted in the S_0 state ($\alpha = 90^\circ$, $\beta \approx 180^\circ$). The latter is responsible for the photochromism of anils and stabilized by steric interactions and rigid media.

Key words: anils, photochromism, TICT, post TICT

Enhancement of Photoacidity by Formation of an Intramolecular Charge Transfer State with Twisted Conformation

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The synthesis of a pair of biphenyls with a cyano acceptor and a hydroxy (methoxy) donor, which differ in the extent of steric hindrance to planarity, induced by ortho-methyl substituents with respect to the phenyl–phenyl bond is described. It is shown that dual fluorescence can be observed, ascribed to a mesomerically stabilized less polar intramolecular charge transfer (MICT) state of near planar geometry, and a more polar one, with strongly decoupled intramolecular CT resembling a TICT state. It possesses an enhanced dipole moment with respect to the MICT state, but considerably deviates from the perpendicular geometry as judged from the transition moments. This concept is used in conjunction with the excited-state proton transfer (ESPT) mechanism. The resulting photoacidity of the compound forming the enhanced ICT is an order of magnitude larger than for the MICT-compound. The mechanistic concept allows the construction of further compounds with still increased photoacidity.

Key words: intramolecular charge transfer excited states, superphotoacidity, 4-cyanophenol, 4-hydroxy-4'-cyanobiphenyls, time resolved fluorescence

The Excited State Relaxation Path of *N,N*-Diethyl-5-cyanopyridine and *N,N*-Diethylbenzaldehyde

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The molecules which possess, as electron donors, dialkylamino groups linked by a single bond with the acceptor subunits undergo fast excited state intramolecular charge transfer (ICT), emitting dual fluorescence in polar solvents. The short and the long-wavelength fluorescence bands are traditionally assigned as F_b and F_a , respectively. The nature of the excited state from which the F_a emission originates, as well as the mechanism of energy degradation have been the subject of many controversies. As the objects of this study, 2-(*N,N*-diethyl)-5-cyanopyridine (**PEC**) and *p*-*N,N*-diethylaminoacetophenone (**DEABA**) were selected. For these molecules different sequence of the two low-lying $\pi\pi^*$ L_a and L_b states was postulated, which can help to verify the excited state mechanisms of the charge separation. The experimental results obtained by stationary and time-resolved spectroscopy show that the anomalous F_a emission originates from the ICT state generated by the mutual twist of the donor and acceptor group (TICT model).

Key words: electron transfer, TICT state, time-resolved spectroscopy

Hydrogen Bonding and Protonation Effects on Excited-state Electron Transfer in *meta*- and *para*-Dialkylaminopyridines

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Synthetic, spectral and photophysical investigations were performed for a series of dialkylaminopyridines (DAAPs) representing electron donor-acceptor systems. 4-Dimethylaminopyridine and its analogues, substituted by an electron donor at the *para* position of the acceptor ring, show solvent-dependent dual luminescence from the substrate (primary excited state) and the product (TICT state) of the photoinduced electron transfer process. The investigations in mixed solvents (*n*-hexane + 1-butanol) allow us to prove that dual luminescence is observed for 1:1 complexes of 4-DAAPs with the alcohol molecule hydrogen-bonded to the pyridine nitrogen atom. Contrary to 4-DAAPs, the electronic structure and geometry of the fluorescent CT state of 3-diisopropylaminopyridine are solvent-dependent (this ¹CT state does not correspond to a full separation of charges). The spectroscopic and photophysical properties of the protonated forms of DAAPs are also presented. It is noteworthy that the monocations of 4-diisopropylaminopyridine exhibit TICT fluorescence.

Key words: dialkylaminopyridines, photoinduced intramolecular electron transfer, dual fluorescence, TICT state, hydrogen bonding and protonation effects

**Photoinduced Intramolecular Charge Separation
and Recombination in a Donor-Acceptor Dyad Linked
via Tetrahedral Carbon Atom.
Photophysics of a Malachite Green Lactone Analogue**

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Lactone forms of triarylmethane dyes (LTAM) with donor-acceptor-donor triad structure undergo ultrafast quantitative intramolecular charge separation (CS) with formation of a highly polar ¹CT state. To clarify the role of the electron donating part in the CS process, 3-methyl-3-(4-dimethylaminophenyl)phthalide (MGLA), an analogue of malachite green lactone (MGL) with only one D part in a D–A dyad structure has been synthesized and its photophysics compared to those of MGL, leucomalachite green (MGH) and malachite green leuconitrile (MGCN). The photoinduced electron transfer processes in MGLA show close analogy with MGL and prove that (i) the tetrahedral carbon atom coupled with C–O bond in quasi-spiro configuration is a very efficient link in ultrafast intramolecular electronic communication and that (ii) the photoinduced charge separation and recombination processes in LTAM molecules involve essentially only one electron-donating group.

Key words: malachite green lactone, 3-methyl-3-(4-dimethylaminophenyl)phthalide, triarylmethane lactones, ultrafast intramolecular electron transfer, solvatochromism of absorption and fluorescence bands

Evidence for Heterolytic Cleavage of C–S Bonds in the Photolysis of 1,3,5-Trithianes

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The homolytic/heterolytic nature of photolytic C–S bond cleavage was studied in 1,3,5-trithianes. The mechanism of photolysis was refined from previous studies. First, evidence was presented for the existence of a precursor of the biradical-like transient (*I*) which itself was identified in previous studies. Second, the nature of *I* was further clarified through methanol-scavenging experiments where the results could be interpreted as lending credibility to the notion that *I* has significant bipolar character. Kinetic and spectral analyses of transient absorptions, following laser excitation of the trithianes, showed that *I* was reacting with methanol. Complementary steady-state photolytic quantum yields supported this finding, and additional, but unidentified, stable products from irradiations in methanol were seen in the HPLC. The formation of these products was interpreted as likely arising from a nucleophilic attack of methanol at the carbocationic end of the bipolar structure of *I*.

Key words: trithianes, C–S bond cleavage, photolysis

Excited-state Solvation of Rhodamines: Dielectric and Specific Contributions

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Primary to tertiary amine based compounds of the form 9'-(2-ester-carbonyl)-phenyl-3',6'-bis-(amino)-xanthylium are studied as models for this class of compounds as regards the $S_1 \leftarrow S_0$ shifts in solution. The magnitude of the solvatochromic shift decreases from primary amine to tertiary amine rhodamine chromophore. Primary amino xanthylium spectral energy at maximum absorption decreases with the solvent electronic polarization whilst it increases with the orientational polarization function, suggesting extensive reorientation in the dipolar moment upon $S_1 \leftarrow S_0$ excitation. By contrast, upon electronic excitation smaller dipolar moment variations are found in N-alkyl rhodamines, respectively with secondary and tertiary amine groups. Primary and secondary amine rhodamines' NH groups establish strong interactions with electron rich atomic centers of solvent molecules increasing the electronic stabilization energy.

Key words: rhodamine, solvatochromism, reaction field, hydrogen bonding

Information Content in Linear Dichroism Spectra

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Spectroscopy with linearly polarized light on aligned samples (LD spectroscopy) is a useful technique that may greatly enhance the possibilities for determining sample structure, making spectral assignments, and several other tasks, generally based on a determination of transition moment directions. However, the technique does not provide the same amount of information in all cases; this depends strongly on the molecular symmetry. The almost ideal case is that of D_{2h} , D_2 , or C_{2v} symmetry, when only 3 different (perpendicular) transition moment directions are possible.

When the molecular symmetry decreases, the information that may be obtained becomes less precise. If the molecule has a plane of symmetry left, the transition moment may be located perpendicular to the symmetry plane or at any direction in the plane, and much useful information may still be extracted.

In the case of a molecule with no symmetry at all the information that can be obtained often becomes highly qualitative, unless special information happens to be available. Unfortunately, this severe limitation is sometimes overlooked when low-symmetry molecules are studied, and the spectra are evaluated the same way spectra for symmetrical molecules are. This is an obvious source of error, and conclusions based on such an analysis are hardly reliable.

In this paper, the spectroscopic technique, assumptions commonly made, and the mathematical treatment of IR and UV spectra are briefly summarized for different molecular symmetries. This is illustrated by a few examples, including new IR LD spectra of limonene, a very difficult, low symmetry case.

Key words: polarization, UV-VIS, IR, LD spectroscopy

The Vibrational Structure of Dibenzo-*p*-dioxin. IR Linear Dichroism, Raman Spectroscopy, and Quantum Chemical Calculations

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The title compound (DD) was investigated by IR and Raman spectroscopy, including FTIR linear dichroism (LD) measurements on samples aligned in stretched polyethylene. The observed IR and Raman wavenumbers, IR polarization directions, and relative intensities were generally well reproduced by the results of a harmonic analysis based on B3LYP/cc-pVTZ density functional theory (DFT). The combined experimental and theoretical results led to proposal of a nearly complete assignment of the fundamental vibrational transitions of DD, involving reassignment of several transitions. The results are consistent with the assumption of molecular D_{2h} symmetry, thereby supporting the conclusion reached earlier by Gastilovich and coworkers.

Key words: dioxins, vibrational transitions, infrared spectroscopy, Raman spectroscopy, linear dichroism, polarization directions, density functional theory

Correlations of Charges of Substituent Active Region in C-substituted Tetrazoles with Their Gas-phase Acidity, Hammett Constants, and Charge Distribution in Tetrazolic Rings

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Electron distribution was investigated in molecules of 5C-substituted tetrazoles by means of Natural Population Analysis. The analysis of the impact of substituents on the excess of π electrons in the ring and on the uniformity of their distribution produced similar results as were recently reported for derivatives of *p*-benzoic acid. The significant correlation coefficients of the two properties with the Hammett constants have been found. The more uniform the π electron distribution, measured by means of standard deviation of π electrons amounts localized on individual atoms in the ring, the more acidic is the molecule. On the other hand, an increase of the π electron number in the ring brings about an opposite effect. No correlation was found between the substituent charges and the Hammett constants. However, a new variable, namely charge of the substituent active region, composed of charge of a substituent added to charge of the ring C_{ipso} atom, was highly correlated with the Hammett constants, as well as with charge of acidic hydrogen of the >N–H group. The results prove that the set of charges of the substituent active region may be perceived as a theoretical equivalent of the experimental set of Hammett constants and that it is closely related to properties of this group of compounds.

Key words: tetrazoles, substituents, Hammett constants, gas-phase acidity, charge distribution, Natural Population Analysis, substituent active region

Proton or Hydrogen Transfer? Charge Distribution Analysis

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The meaning of terms “proton transfer” (PT) and “hydrogen transfer” (HT), commonly encountered in the literature, is not always unambiguous, especially in the case of intramolecular tautomerization processes. Depending on the used criterion, the same reaction may be classified as either PT or HT. Two criteria for distinguishing between PT and HT are discussed: (a) formal translocation of charge; (b) the reaction mechanism, in particular the coupling between the motion of the proton and the electron density redistribution. The analysis is illustrated using the values of ground and excited state partial charges calculated for three well-known examples of molecules that undergo photo-induced and/or ground state tautomerization: 2-hydroxyacetophenone, 2,2'-bipyridyl-3,3'-diol, and porphycene.

Key words: proton transfer, hydrogen transfer, charge distribution