The kinetics of hydrogen exchange in molecular systems with H-bonds studied by kinetic IR spectroscopy and low-temperature NMR spectroscopy methods is critically reviewed. The experimental rate constants and activation energies obtained so far for molecules capable of forming H-bonds as both proton donors and proton acceptors are collected and analyzed from the point of view of the influence of H-bond formation ability of the molecules-partners. The evidence available testifies to a molecular mechanism of the H-exchange reactions in inert solvents and in the gas phase via the formation of cyclic, mostly bimolecular, intermediates. The different mechanisms of the molecular H-exchange process in inert media are discussed and the possible paths of experimental elucidation of reaction mechanism are offered.
Hydrogen Bonds in the 1:1 and 2:1 Complexes of Trigonelline with Mineral Acids Studied by FTIR, $^1$H and $^{13}$C NMR Spectroscopies

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The 1:1 and 2:1 complexes of trigonelline (TRG) with HBr, HI, HNO$_3$, HClO$_4$ and HBF$_4$ have been synthesized and their FTIR, $^1$H and $^{13}$C NMR spectra were analyzed. The 1:1 complexes are divided into two groups. The first group includes complexes with HBr, HI and HNO$_3$, in which a proton is transferred from the acid to TRG and the anions are bonded with the carboxylic group, COOH···X$^-$ (1). The second comprises complexes with HClO$_4$ and HBF$_4$, with two molecules of protonated TRG forming dimer, like benzoic acid, and the anions interacting exclusively with the positively charged nitrogen atoms (2). All 2:1 complexes crystallized with one water molecule and their FTIR spectra are of Had Citype iii, characterized by an intense broad (continuum) absorption below 1600 cm$^{-1}$ typical of a short-strong hydrogen bond (SSHAB) with a delocalized proton and a single νC=O band.

In these complexes the water molecule interacts electrostatically with one positively charged nitrogen atom and the anions with the second one (3). The water molecule additionally forms a hydrogen bond with Br, I and NO$_3$ ions. The proton and carbon chemical shifts of the complexes in D$_2$O have been determined and discussed.

Quantum-Chemical Calculations of First-Order Hyperpolarizability of Epoxy Oligomers with Chromophore in the Main Chain

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Results of quantum-chemical calculations of first hyperpolarizabilities for a number of epoxy oligomers with nonlinear optical (NLO) chromophores incorporated into the main chain as a side group are presented. These oligomers simulate the internode chains of cross-linked NLO materials, which are the most promising candidates for application in optoelectronics. The attempt is made to establish a relationship between the hyperpolarizability and the conformation of the bearing chain in the vicinity of the chromophore. The structure and conformation of the oligomer chain are shown to affect significantly the longitudinal hyperpolarizability of the chromophore. Some recommendations are given to obtain hyperpolarizability values optimal for the studied molecular systems.
Relationship Between Electronic Structure and Nonlinear Optical Activity of Push-Pull Polyenes: Step Towards a Quantitative Treatment

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Mesomeric effect of substituents in stereoregular push-pull polyenes has been studied, bond length alternation being used for the monitoring of π-electron displacement along the polyene segment. Quantitative calibration of the π-donor and π-acceptor strength of various substituents has been performed with the special scale of substituents mesomeric constants. A simple quantum chemical technique for estimation of mesomeric constants has been developed. A simple additive equation describing the substituents mesomeric effect on bond length alternation in push-pull polyenes has been elaborated. Specific push-pull effect has been demonstrated to be the essential feature of push-pull polyenes. A qualitative relationship between the suggested mesomeric constants and longitudinal hyperpolarizability has been established.
IR $\nu$(OH) Band and Dimerization of Phosphorus Acids
in the Gas Phase and Solid State

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The infrared absorption spectra of phosphorus acids $R_2$POOH ($R = H, CH_3, CH_3Cl, CH_3I,
C_6H_5, C_3F_7, CH_3O, C_4H_9O$) have been recorded in the gas phase and in the solid state in
the range 4000–1000 cm$^{-1}$. The equilibrium between monomers and dimers of $R_2$POOH
was studied in the gas phase between 400–650 K. The broad absorption band of the
$\nu$(OH) stretching vibration of the cyclic dimer in the region 3600–900 cm$^{-1}$ is registered
in the gas phase spectra at 400–600 K and in thin films spectra at 90–300 K. In all cases
the band has the characteristic ABC structure, typical for spectra of complexes with
strong hydrogen bond in the crystal phase and solution. The intensity and the first and
second spectral moments of this band were determined. It was found that, on passing
from thin films at low temperature to the gas phase at high temperature, the redistribution
of intensity from the low frequency wing to the high frequency wing takes place. Despite
significant differences of dimerization enthalpies (20–60 kcal/mole), the spectra of all
acids have similar structure and close values of spectral moments, although the values of
intensities are different.
Phenol: A Succinct Essay About Its Bonding Ability in Three Examples

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The present essay represents an effort to focus on some aspects of the bonding abilities of phenol throughout a theoretical study of the three potential energy surfaces of the interaction of phenol with the HCN, HOCN, and HF (including HCl) molecules. The studied surfaces clearly demonstrate the existence of the alternative bonding of phenol via its $\pi$ cloud, largely localized in the vicinity of the para carbon atom, leading to the formation of metastable $\pi$ hydrogen-bonded complexes with sufficiently large lifetimes comparable with experimental timescales.

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The topological space of the glycine–uracil complex has been scanned at the semi-empirical PM3 level of theory and the lowest energy complexes have been characterized at the B3LYP/6-31++G** level. These complexes are characterized by two hydrogen bonds, in which the carboxylic group of glycine interacts with proton donor and acceptor sites of uracil. The stabilization energy for three complexes, with the NH⁻⁻O and O⁻⁻HO hydrogen bonds each, spans a narrow range of 15.6–12.3 kcal/mol. The fourth complex with one strong O⁻⁻HO and one weak CH⁻⁻O hydrogen bond is bound by 10.2 kcal/mol.
Angular Group Induced Bond Alternation (AGIBA).
Part VIII. Crystal and Molecular Structure of 2,3,6,7-Tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine. A Competition Between the AGIBA and the Through Resonance Effects

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Low temperature (100 K) X-ray diffraction study of 2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinoline-9-carbaldehyde(E,E)-azine provided the molecular geometry allowing to study a competition between the AGIBA and through resonance effects. The simplified derivatives, for which geometry was obtained by optimization at B3LYP/6-311G** level of theory, supported the results for the title compound and the conclusion that the AGIBA effect and the through resonance may exist simultaneously in systems with appropriate substituents.
Quantum-Chemical Study with Application of the PCM Model on Correlation Between Biological Activity and Molecular Structure of 5-Amino-3-methylisoxazole-4-carboxylic Acid Hydrazide Schiff Base Derivatives

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Theoretical calculations on 5-amino-3-methylisoxazole-4-carboxylic acid hydrazide Schiff base derivatives using Polarizable Continuum Model in order to account for water solvation effects are presented. The compounds studied exhibit biological (immunosuppressing or immunostimulating) activity, measured experimentally in various assays. The quantum chemical DFT calculations are used to obtain electronic descriptors of molecular structure. These descriptors, together with other physicochemical parameters, are used to derive quantitative relationships between the structure and the biological activity.
Excited State Intramolecular Proton Transfer in 9-Oxo-9,10-dihydro-acridine-4-carboxylic Acid. Photophysical and Computational Studies

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9-Oxo-9,10-dihydro-acridine-4-carboxylic acid in both methanol and acetonitrile possesses a dual fluorescence and complex fluorescence intensity decay, whereas 9-oxo-9,10-dihydro-acridine-2-carboxylic acid shows only one emission band and monoexponential fluorescence intensity decay. Theoretical calculations, using a semiempirical PM3 method, confirm, in the case of 9-oxo-9,10-dihydro-acridine-4-carboxylic acid, the excited state intramolecular proton transfer process from nitrogen atom to the oxygen of carbonyl of the carboxylic group.
FT-IR Studies of CH…B Interactions in Fluoroform Containing Cryosolutions

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A transition from a blue shifted frequency of the ν₁ band of CF₃H to a conventional red frequency shift, accompanied by unusually varying integrated intensity of the corresponding ν₁ band, have been studied in CF₃H/B systems, where B = Ar, N₂, CO, CO₂, O(CD₃)₂, NH₃, and N(CD₃)₃. DFT/B3LYP and ab initio MP2 calculations, utilizing the 6-311++G(3df,3pd) basis set, predict a weakly H-bond-like linear F₃CH…B complex formation in the series studied and reproduce experimentally observed variations of spectroscopic parameters. The results obtained are treated in the framework of induced dipole moment, taking into account opposite directions of the CH bond dipole moment and the dipole moment of the whole molecule. In the range of overtone and combination bands of fluoroform, new weak bands have been detected. They were attributed to simultaneous excitations of vibrations of interacting CF₃H and B (= CO, CO₂) molecular pairs.

Excited-State Proton Transfer Reaction in a New Benzofuryl 3-Hydroxychromone Derivative: The Influence of Low-Polar Solvents

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Unique properties of a new 3-hydroxychromone derivative 2-(6-diethylamino-benzol[b]furan-2-yl)-3-hydroxychromone (FA) in its ability to exhibit excited-state intramolecular proton transfer (ESIPT) reaction are described. In contrast to all other chromone and flavone derivatives studied, in low-polar solvents it exhibits in emission, together with the tautomer (T*) band, an intensive band of the normal (N*) form. Previously the intensive N* form in emission was observed only in highly polar, mostly protic solvents. While its absorption spectra are sensitive to H-bond acceptor properties of the solvent, the fluorescence spectra are not. This suggests that intermolecular H-bonds with a solvent, if they exist in the ground state, are reorganized in the excited state in favor of intramolecular bond, which is the pathway for ESIPT reaction. The energy difference, \( \nu_{N^*} - \nu_{T^*} \), between N* and T* emission maxima is in almost ideal correlation with the Reichardt solvatochromic parameter \( E^T \). This suggests the use of FA as a highly sensitive polarity sensor. A good correlation between \( \nu_{N^*} - \nu_{T^*} \) and the ratio of the N* and T* band intensities is observed. This allows to observe the solvent effects on a manifold increased level of sensitivity. The analysis based on Lippert and Bakhshiev equations and the quantum-chemical calculations suggest a substantial increase of the dipole moment on electronic excitation to the N* state. The appearance of the N* form in emission may be the result of its dielectric stabilization.
Spectral Properties of Phenylbenzopyrylium Salts in Solutions as a Result of Their Nucleophilic Solvation

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A dependence of spectral properties of 2-phenylbenzopyrylium (PBP) salts in solutions on the solvent nucleophilicity is presented. A simple solvate complex model for quantum chemical estimation of the nucleophilic solvation influence on band positions in absorption and fluorescence PBP salt spectra is proposed. Quantum yield changes of the PBP salts in solvents of different nucleophilicity are explained as due to the influence of nucleophile solvation on the efficiency of the intersystem crossing in PBP cations. Two ways of this influence are proposed: the direct one, due to energy changes in S1 and T1 levels, and the indirect one, due to an increase or decrease of spin-orbital interaction efficiency, caused by changes of the structural rigidity of solvated PBP cations.
Kinetics of the Reaction Between Ethylallyl Ethylacrylate and tert-Butyl Hydroperoxide in the Presence of Molybdenum Catalysts

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The reaction of ethylallyl ethylacrylate with tert-butyl hydroperoxide in the presence of molybdenum catalysts (Mo₂B and Mo₂Bₓ) was studied. The general kinetic model for the process is proposed, which adequately explains the hydroperoxide consumption up to 80% conversion. The equilibrium constants of the complex formation were calculated. It was shown that Mo/B ratio in the catalyst affects the catalyst–hydroperoxide complex stability.
The Role of Hydrogen Bonds in the Pressure-Induced Structural Distortion of 4-Hydroxyacetanilide Crystals

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Results of X-ray diffraction and IR-spectroscopy studies of the role of hydrogen bonds in the structural distortion of the monoclinic and the orthorhombic polymorphs of paracetamol induced by hydrostatic pressure (up to 4-5 GPa) are analyzed. Two groups of phenomena were studied: (i) the anisotropic structural distortion of the same polymorph, (ii) transitions between the polymorphs induced by pressure. The bulk compressibilities of the two polymorphs are practically equal. The anisotropy of pressure-induced structural distortion is qualitatively different. Lattice expansion in particular crystallographic directions was observed for the monoclinic polymorph. With increasing pressure the intermolecular NH...O and OH...O hydrogen bonds contracted and the intramolecular angles between the planes of the phenyl ring and the acetamide group decreased. Pressure-induced transitions between the polymorphs were poorly reproducible and limited by nucleation of the new polymorph.
Interactions, Stabilizing the Structure of Intermolecular Polycomplex Between Poly(vinyl alcohol) and Poly(acrylamide)

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The structure and properties of the intermolecular polycomplex, formed by cooperative intermolecular hydrogen bonds between poly(vinyl alcohol) and poly(acrylamide), were investigated. By viscometry, gel chromatography and differential scanning calorimetry the characteristic composition of polycomplex was established. The compatibility of polymers and structural peculiarities of polycomplex in a block state were characterized. Due to computer processing of the polycomplex IR spectra in amide I, amide II region by the spline method, the presence of the absorption band at 1668 cm⁻¹, related to hydrogen bonds between polymer pair, was shown. The developed hydrophobic regions in polycomplex structure in water, which additionally stabilize the polycomplex particles, were detected. The structure of such intermolecular polycomplexes is proposed.
Interpretation of Vibrational Spectra of Liquid Water

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Based on Raman spectral studies of H2O, D2O, HOD and aqueous solutions of various salts we suggest a new interpretation of vibrational spectra of liquid water. The striking result is obtained that a quite definite set of weak H-bonds corresponds to a quite definite set of the rotational reorientations of the water molecules. The contribution of each orientation depends on the temperature and on the nature of the solved salts.