

## Synthesis, Crystal Structure and Properties of Tetra(piperidinium)bis(ethanolate) Decavanadate

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The title compound,  $[(C_5H_{12}N)_4][V_{10}O_{26}(OC_2H_5)_2]$  consisting of a  $[V_{10}O_{26}(OC_2H_5)_2]^{4-}$  polyanion and four protonated piperidinium  $[C_5H_{12}N]^+$  was synthesized and characterized by elemental analyses, spectroscopic (IR, UV-vis and ESR) studies and single-crystal X-ray diffraction. It crystallizes in the monoclinic system, space group  $P2_1/n$  and  $Z = 2$ , with  $a = 10.628(2)$  Å,  $b = 12.983(2)$  Å,  $c = 16.160(3)$  Å, and  $\beta = 90.74(3)^\circ$ . Least-squares refinement gave a final R factor of 0.0559 for 4024 unique reflections having  $I > 2\sigma(I)$ . A three-dimensional supramolecular arrangement of the polyanion and piperidinium cations in the crystal lattice is generated by hydrogen bonds. In contrast with other anionic decavanadates, there are two ethoxy groups bridging the outmost vanadium atoms in the title compound. The coordinated nature of the ethoxy-bridge is the first example among the reported decavanadates. The cyclic voltammetry behaviour of the compound is preliminarily investigated.

**Key words:** decavanadate, ethoxy-bridge, piperidinium ion, crystal structure, cyclic voltammetry

## **Synthesis, Thermal Decomposition, Magnetic Properties and Biological Activities of Co(II), Ni(II), Cu(II) and Cd(II) Complexes of Some Triazole-3-thione Schiff Bases**

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A series of novel complexes of 4-amino-5-benzyl-4H-1,2,4-triazole-3-thione (ABT), 5-benzyl-4-(benzylideneamino)-4H-1,2,4-triazole-3-thione (BBT), 5-benzyl-4-[(2-hydroxybenzylidene)amino]-4H-1,2,4-triazole-3-thione (HBHT) and 5-benzyl-4-[(4-methoxybenzylidene)amino]-4H-1,2,4-triazole-3-thione (BMT) with the divalent ions Co(II), Ni(II), Cu(II) and Cd(II) have been prepared by direct combination of the ligand and metal chloride salt in ethanol. The structures were determined by elemental analysis, molar conductance, magnetic measurements, thermal behaviour, infrared and electronic spectral data. ABT involves N (amino group) and S donor atoms, BBT and BMT involve N (azomethine) and S donor atoms, both act as neutral bidentate ligands. HBHT involves N, O and S donor atoms, acting as monobasic tridentate ligands. The stoichiometry of these complexes is M:L = 1:1 and/or 1:2. The geometry of the complexes was assigned on the basis of magnetic and electronic spectral data. Tetrahedral and octahedral structures were proposed for the metal complexes. The ligands and their complexes were screened for their antibacterial activity.

**Key words:** triazole thione Schiff base complexes, synthesis, characterization, antibacterial activity

## Nucleophilic Cleavage of Selenaheterocyclic Ring in Benzisoselenazol-3(2*H*)-ones and 1,3,2-Benzodiselenazoles

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The reactions of cyclic selenenamides: benzoselenazol-3(2*H*)-ones and 1,3,2-benzodiselenazoles **3** with living cell nucleophiles such as water and thiols were investigated. Both of them caused Se–N bond cleavage. The thiolysis of **1** led to selenosulphides **6**, **9** or to products of their disproportionation the equimolar mixtures of diselenides **7** and disulphides **8**. The hydrolysis of **1** and **3** as well as thiolysis of **3** resulted in formation of corresponding diaryl diselenides **7** or **10**.

**Key words:** selenium compounds, thiolysis, hydrolysis, selenaheterocycles, selenosulphides

## Synthesis of 1,3-Oxaselenan-2-imines from Isoselenocyanates

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The reactions of aryl isoselenocyanates **1** with 3-chloropropan-1-ol (**8**) in the presence of sodium hydride in dichloromethane at room temperature gave 1,3-oxaselenan-2-imines **10** in fair yield. A reaction mechanism *via* nucleophilic attack of the alcoholate at the isoselenocyanate **1**, followed by an *6-exo-tet* cyclization, is most likely.

**Key words:** isoselenocyanates, 1,3-oxaselenan-2-imines, selenaheterocycles, cyclizations

## Synthesis of 2-(4-Chloro-2-mercaptobenzenesulfonyl)-3,5-dihydroxy-1,1-dioxo-2H-1,2,4,6-thiatriazine Derivatives with Potential Anti-HIV and Anticancer Activities

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Several 2-(4-chloro-2-mercapto-5-R-benzenesulfonyl)-3,4-dihydroxy-1,1-dioxo-2H-1,2,4,6-thiatriazines (**9–12**) have been synthesized as potential anti-HIV (**9–10**) or anticancer (**11–12**) agents. The *in vitro* anti-HIV or antitumor activities were tested at the US National Cancer Institute (Bethesda, MD), and the structure-activity relationships are discussed. Compound **9** (R = Me) showed good anti-HIV activity with 50% effective concentration (EC<sub>50</sub>) value of 73.2 μM and moderate cytotoxic effect (IC<sub>50</sub> = 220.0 μM). The compounds **11** and **12** exhibited high or reasonable activity against most (98%) of the human tumor cell lines tested. Compound **12** (R = 4-ClC<sub>6</sub>H<sub>4</sub>NHCO) is the prominent of the compounds due to its good activity against 54 human tumor cell lines (GI<sub>50</sub> = 0.67–38.9 μM), and remarkable selectivity toward renal cancer RXF 393 cell line (GI<sub>50</sub> = 0.67 μM).

**Key words:** 2-(4-chloro-2-mercapto-5-R-benzenesulfonyl)-3,4-dihydroxy-1,1-dioxo-2H-1,2,4,6-thiatriazines, synthesis, anti-HIV and antitumor activities, structure-activity relationships

## Butyrylcholinesterase Inhibitory Triterpenes from *Salsola baryosma*

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Salsolic acid (**1**), a new oleanane type triterpene has been isolated from the chloroform soluble fraction of *Salsola baryosma* along with known triterpenes (**2**) and (**3**) isolated for the first time from this species. The compounds **1–3** showed inhibitory activity against the enzyme butyrylcholinesterase.

**Key words:** *Salsola baryosma*, Chenopodiaceae, triterpenes, butyrylcholinesterase inhibition

## Synthesis, and *In Vitro* Antitumor Activity of a New Series of 4-Chloro-2-mercapto-5-methylbenzenesulfonamide Derivatives

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The synthesis of *S*-(5-chloro-4-methyl-2-sulfamoylphenyl) *N*-(phenylsulfonyl)benzothiohydrazonates **4a–k** is described. The compounds **4b–f** and **4j–k** were screened at the US National Cancer Institute for their *in vitro* activities against a panel of 53–57 human tumor cell lines and relationship between structure and antitumor activity is discussed. The compound **4b** was inactive, whereas the remaining compounds exhibited fairly high or reasonable activity ( $GI_{50} = 8.12–24.9 \mu\text{M}$ ) against one or more human tumor cell lines.

**Key words:** *S*-(5-chloro-4-methyl-2-sulfamoylphenyl) *N*-(phenylsulfonyl)benzothiohydrazonates, synthesis, antitumor activity

**Synthesis and Properties of Azoles and Their Derivatives.  
Part LVIII. DFT Study on [2+3] Cycloaddition of  
*trans*-Nitroethenes to *Z*-C,N-Diphenylnitrone**

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DFT calculations indicate that the transition states of [2+3] cycloaddition of *trans*-2-phenylnitroethene to *Z*-C,N-diphenylnitrone led to 3,4-*cis* and 3,4-*trans* 4-nitroisoxazolidines are almost perfectly symmetrical. Asymmetry of the transition states appears for the reaction with more  $\pi$ -deficient *trans*-2-(trichloromethyl)-nitroethene. Nevertheless, in both cases the formation of azolidine rings occurs in one step. The calculational results correlate well with experimental data.

**Key words:** DFT calculation, nitroalkene, nitrone, [2+3] cycloaddition

## **<sup>1</sup>H NMR, <sup>13</sup>C NMR and Computational DFT Study of the Structure of 2-Acylcycloalkane-1,3-diones in Solution**

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<sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-acylcyclopentane-1,3-dione [acyl = formyl (**1**); acetyl (**2**)] and 2,6-dioxocyclohexanecarboxylic acid (**3**) have been measured. The optimum molecular structures of *endo*- and *exo*-enolic forms of investigated objects in solution have been found using DFT method with B3LYP functional and 6-311G(2d,p) basis set. The theoretical values of the NMR parameters have been then calculated using GIAO-DFT method with the same functional and basis set. The theoretical data obtained for compounds **1–3** have been used to interpret their experimental NMR spectra in terms of the equilibrium between different tautomers. It has been found that for investigated triketones an *endo*-tautomer overwhelmingly prevails.

**Key words:** triketones, NMR, DFT study, tautomerization

## **Investigation of Asymmetric Michael Addition of Meldrum Acid to Conjugated Nitroalkenes Carried out in the Presence of Chiral Amines**

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Nitroalkenes reacted with Meldrum acid in the presence of chiral amines to give the adducts in high yields and limited enantiomeric excesses. The highest enantioselectivity was reached at 20°C in the presence of cinchona alkaloids (*ee* = 20–25%). Unexpectedly, *ee* of the product was decreased by temperature lowering.

**Key words:** Meldrum acid, nitroalkenes, asymmetric Michael addition

## An Attempt for Elucidating the Cause of Distortion of Cyclohexane Elution Peaks from Heterogeneous Carbon Materials

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It was noticed, that during the elution of cyclohexane from some active carbons at 563–583 K, distorted peaks were obtained. *Gram-Charlier* type A and *Edgeworth-Cramér* series unsuccessfully described the distortion of peaks. An attempt has been made to elucidate the cause of the distortion by smoothing the peaks employing the *Savitzky-Golay*'s and the *loess* procedures. The curvatures of the first and the second derivatives were analyzed. The subtle energetic stereoeffects in the distribution of cyclohexane and suitable architectonics of energetic centres seem to be the causes of the peak distortion.

**Key words:** distorted peaks in gas chromatography, displacement and tag-along effects, *Gram-Charlier* type A and *Edgeworth-Cramér* series, *Savitzky-Golay*'s and the *loess* procedures, XPS, XRD and AFM tests

## **Kinetics and Mechanism of the Nucleophilic Cleavage of Disulfide Bond in 2,2'-Dithio-diimidazoles with Hydroxide Ions**

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Kinetics of the cleavage of disulfide bond of dithiobisdisulfides of diimidazoles to their parent imidazoles by hydroxide ion have been investigated spectrophotometrically. Rate equation and other observations suggest that the nucleophilic attack of hydroxide ion on one of the sulfur atoms of disulfide bond is a rate limiting step. This process is accompanied by much slower, parallel reaction with water as a nucleophile. Hence the full kinetic equation for nucleophilic cleavage of 2,2'-dithio-diimidazoles in aqueous alkaline solutions is a two-term equation:  $-(d[\text{RSSR}]/dt) = k_1[\text{RSSR}][\text{OH}^-] + k_2[\text{RSSR}][\text{H}_2\text{O}]$ , where  $k_1 > k_2$ . The mechanism of the reaction is proposed.

**Key words:** dithio-diimidazoles, nucleophilic cleavage, hydroxide ion, reaction mechanism

## Experimental and Theoretical Study on 3-Benzyl-4-phenyl-1,2,4-triazole-5-thione

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The 3-benzyl-4-phenyl-1,2,4-triazole-5-thione was synthesized and examined by elementary analysis, IR and electronic spectra. Density functional theory calculations of the structure, natural bond orbitals and thermodynamic functions of the title compound were performed at B3LYP/6-311G\*\* level of theory. Vibrational frequencies were predicted, assigned and compared with the experimental data, and they are supported by the experimental data. Electronic absorption spectra were calculated by the time-dependent density functional theory (TD-DFT), which indicates that the two absorption bands are mainly derived from the contribution of bands  $\pi \rightarrow \pi^*$ . The calculation of the second order optical nonlinearity was carried out, giving value of molecular hyperpolarizability equal to  $4.025 \cdot 10^{-30}$  esu. These calculated results were also compared with results obtained for a similar molecule, 4-phenyl-3-[(1,2,4-triazol-1-yl)methyl]-triazole-5-thione, reported earlier by this group.

**Key words:** density functional theory, vibrational frequencies, electronic absorption spectra, second order optical nonlinearity

## **Studies on the *N*-Lauroyl-*N*-methylglucamide Based Microemulsion with $\epsilon$ - $\beta$ Fishlike Phase Diagram**

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The microemulsion phase behavior of the quaternary system of *N*-lauroyl-*N*-methylglucamide (MEGA-12)/alcohol/*n*-octane/water was studied with a  $\epsilon$ - $\beta$  fishlike phase diagram. The composition of the balanced interfacial layer was calculated by the  $\epsilon$ - $\beta$  hydrophile-lipophile balanced (HLB) plane equation. The physicochemical parameters of the system were also obtained. The solubilization power was discussed.

**Key words:** microemulsion, fishlike phase diagram, solubilization, *N*-lauroyl-*N*-methylglucamide

## Experimental and Density Functional Studies on Two Substituted 1H-Benzimidazoles

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Two substituted 1H-benzimidazoles, 2-(4-chlorophenyl)-1H-benzimidazole and 1-(2-chlorobenzyl)-2-(2-chlorophenyl)-1H-benzimidazole, have been synthesized and characterized by elemental analysis, IR and UV-Vis spectra. An extended MO calculations using density functional theory (DFT) at B3LYP/6-311G\*\* level have been carried out on the two compounds. Comparison of the experiments with the calculated results suggests that the optimized geometries can well reproduce the molecular structures. Atomic charge distributions show that both of the title compounds are potential ligands to coordinate with metallic ions. Natural population analyses indicate that the electronic transitions corresponding to electronic spectra are mainly derived from the contribution of bands  $\pi \rightarrow \pi^*$ . Thermodynamic properties of the two title compounds at different temperatures have also been calculated on the basis of vibration analyses.

**Key words:** DFT calculations, atomic charge distributions, electronic spectra, thermodynamic property

## Chlorine Removal from 1,2-Dichloroethane over Ni/C Catalysts

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Active carbon-supported nickel catalysts prepared from nitrate and sulfate nickel salts have been investigated in the hydrodechlorination of 1,2-dichloroethane at 210–230°C. The ex-sulfate catalyst showed practically 100% selectivity towards ethene. In contrast, the ex-nitrate sample, which additionally has been subjected to a high temperature pretreatment exhibited a steadily increasing selectivity towards vinyl chloride (up to 11%), resembling the catalytic behavior of previously investigated Ni/C catalysts characterized by low metal dispersions. The X-ray diffraction study of reduced and used catalysts as well as the temperature programmed hydrogenation of deposited coke from used catalysts showed a different extent of nickel carbiding during hydrodechlorination. The presence of residual sulfur in the ex-sulfate catalyst clearly inhibits carbon incorporation into nickel.

**Key words:** 1,2-dichloroethane, Ni/C catalyst, hydrodechlorination, selectivity to ethene, selectivity to vinyl chloride, catalyst carbiding

**Stability of  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  Complexes with Valinomycin in Nitrobenzene Saturated with Water**

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