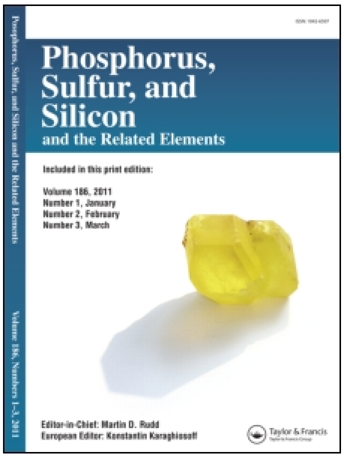

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SYNTHESIS AND INVESTIGATION OF NEW TETRATHIAFULVALENES ABLE TO FORM INTERMOLECULAR HYDROGEN BONDS OF THE NUCLEIC ACIDS BASE PAIRS TYPE

OJĀRS NEILANDS, VIJA TĪLIKA, ZANDA CELMIŅA, ALMA EDŽIŅA
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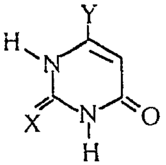
Abstract. The synthetic methods are worked out for preparing of 2,4-dioxopyrimido- and 2,4- aminooxopyrimidotetrathiafulvalenes. Redoxproperties and formation of charge transfer complexes and cation-radical salts are investigated. X- ray crystal structure confirm formation of dimers by means of hydrogen bonds.

Tetrathiafulvalene (TTF) derivatives have played an important role in the development of organic conductors and are the main matter for organic superconductors.[1] Very few examples of TTF able to form intermolecular hydrogen bonds (HB) are known. The ability to form HB could be of crucial importance for on efficient intermolecular interaction and increasing of conductivity of the cation radical salts.

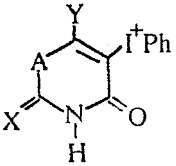
We have set up the goal to synthesize TTF able to form two or three strong HB, therefore the choice fell on the derivatives containing moieties of uracil, guanine, cytosine or adenine.

The key molecules for synthesis are barbituric acid **1a** or its aminoderivatives **1b,c**. Treatment of **1** with diacetoxyiodobenzene gives the 5- phenyliodonium betaines **2**. Nucleophilic attack of **2** with sodium diethyldithiocarbamate[2,3] affords the desired **3**, which cyclisation gives the novel heterocyclic system **4**, Z= $NEt^{+}_{2}ClO^{-}_{4}$ (in case of **3**, X= O, Y= AcNH).

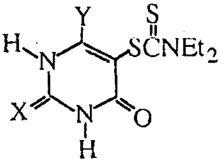
The interaction of the perchlorates **4** with sodium sulfide or selenide results in a two step synthesis[2,3] the thiones **4**, Z= S, or selones **4**, Z= Se. Compounds **4a** are acids (pK_1= 4.8...5.5 in H_2O).[4] In crystals and solutions **4a** exists in a dioxostructure. The selones **4** are the starting compounds for synthesis of new TTF. The little soluble red selones form in reaction with bis- (trimethylsilyl) acetamide in benzene a well soluble product, which is used immediately in the coupling reaction with the substituted 1,3- dithiole -2- selones in presence of triphenylphosphine.[5] In this manner the TTF **5**[6] and **6** are synthesized (yield is 29...50 %).



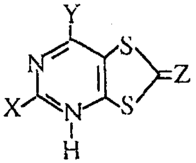
1. a X= O, Y= OH
b X= NH, Y= OH
c X= O, Y= NH_2



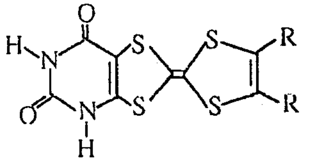
2. a A= NH, Y= O^-
b A= NH, Y= O^-
c A= N, Y= NH_2



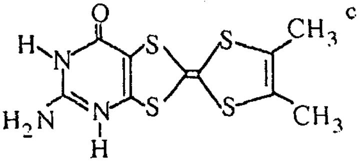
3.



4. Z= NEt_2ClO_4 , S, Se
a X=Y= OH
b X= NH_2, Y= OH
c X= OH, Y= NH_2



5. a R= CH_3
b RR= SCH_2CH_2S
c R= SCH_3



6.

The crystallization of **5a** from DMF:H_2O (96:4) gives orange crystals **5a**·DMF suitable for X- ray analysis. Two molecules of **5a** form dimers by means of two equal HB NH···O, the distance NH···O is 2.85 Å. There is strong stacking interaction between molecules in the crystal.

The new TTF undergo two reversible oxidation's, for **5a** E_1= 0.72 V, E_2= 0.93 V, for **6**, E_1= 0.56 V., E_2= 0.94 V (CH_3CN, versus Ag/AgCl). We have been able to prepare green salt **5a**·ClO_4 and a new cation radical inner salt of **5a** as well as black complexes **5a**·I_3 and **6**·$I_{0.4 \div 0.5}$.

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