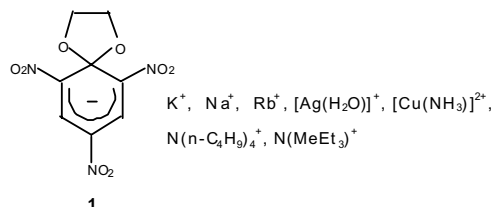


s2.m1.p9 Influence of Cation on Molecular and Electronic Structures of Meisenheimer Complexes. Theoretical Topological Analysis of Electron Density Function. O. Ya. Borbulevych, M.Yu. Antipin, O.V. Shishkin, *X-ray structural Center, Institute of Organoelement Compounds, 28 Vavilov St., Moscow 117813, Russia; SRD Alkali Halide Crystals, STC «Institute for Single Crystals», National Academy of Sciences of the Ukraine, 60 Lenina ave., Khar'kov 310001, Ukraine.*
 Keywords: Meisenheimer complexes, ab intion calculations, Bader's topological theory.

Anionic σ -complexes or Meisenheimer complexes (MC) are very important class of compounds that are a key intermediate in nucleophilic aromatic substitution reactions forming the backbone of numerous important syntheses of pharmaceuticals and potential drugs and several other classes of bioactive agents¹. Our previous investigations^{2,3} of an electron density distributions in MC have shown noticeable potassium cation impact on this distribution. Now we report an explicit study of an influence of cations on molecular and electronic structures of MC.

For the purpose of the current research structures of several Meisenheimer complexes — derivatives of 2,4,6-trinitrobenzene **1** with different cations have been investigated by X-Ray methods.

In addition, a full optimisation of molecular structure of various complexes of anion **1** — X^+ ($X^+ = K^+, Na^+, Li^+, NH_4^+$)



with different coordination of the cation to oxygen atoms has been calculated at the HF/6-31+G* and B3LYP/6-31+G* level of *ab initio* methods which is a attempt of simulation and establishment of ion pair structures in a solution. The coordination of cation gives rise drastic changes of MC geometry as compared with isolated anion which correspond to considerable increase of relevant resonance form contribution to the structure of MC. Moreover, features of electron density distribution in these optimized structures have been revealed using Bader's topological theory.

s2.m1.p10 Topological analysis on intermolecular interaction of two ferromagnetic organic radical molecules. J.-J. Lee and Y. Wang. *Department of Chemistry, National Taiwan University, Taipei, Taiwan.*
 Keywords: charge spin densities.

Electron density studies of two organic radical species, para-nitronyl-4-benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl **1**, and para-bromide-4-benzylideneamino-2,2,6,6-tetramethylpiperidin-1-oxyl **2**, have been carefully investigated by X-ray diffraction method at low temperature(125 K and 100 K).

These two compounds are found to be weakly ferromagnetic with Weiss Constant = 0.37 K and 0.32 K respectively, and with effective magnetic moment of 1.6 B.M. at 298 K. The ferromagnetism of these two compounds is believed to be due to the intermolecular hydrogen bond, N-O...H-C. For example, **1**, the distance between O1...H and O1...C are 2.423(1) Å and 3.414(2) Å, the angle <O...H-C is 151.96(8)°. Topological property analyses give a direct evidence for such intermolecular interactions, the $\rho(r_c)$ (total electron density on the critical point)is 0.04 eÅ⁻³ and $L=0.80$ eÅ⁻⁵ ($L=\nabla^2\rho(r_c)$) which is in accord with values observed elsewhere. This intermolecular hydrogen bond can be classified as close shell interaction .

According to the result of the three MO calculations (Gaussian, Gaussian/DFT, DFT/Dmol), The SOMO(single occupied MO) are mainly contributed from the π -orbital of the nitroxide group and significant spin density is located at the nitroxide group. The spin density lobe of nitroxide group is perpendicular to the N-O bond and is directly pointed toward the hydrogen atom of the phenyl group. In addition, π character radical is evidenced from EPR measurement by the small isotropic nuclear coupling constant of nitrogen of 16. gauss. the DFT/Dmol Calculation performed on the dimer of the radicals show there exist significant spin density population on the hydrogen-bonded hydrogen.

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