

Electron localization function (ELF) study on intramolecular delocalization of the electron density in the H_2X , $H_2C=X$ and XO_2 ($X = O, S, Se, Te$) molecules: Role of the atomic core and lone pair

Slawomir Berski *, Grzegorz Gajewski, Zdzislaw Latajka *

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, 50-383 Wrocław, Poland

Received 13 March 2007; received in revised form 15 May 2007; accepted 15 May 2007

Available online 27 May 2007

Dedicated to Professor Lucjan Sobczyk on the occasion of his 80th birthday.

Abstract

A nature of the chemical bond and delocalization of the electron density in the H_2X , $H_2C=X$ and XO_2 ($X = O, S, Se$ and Te) molecules is systematically studied by means of the topological analysis of the electron localization function (ELF). The covariance parameter $\text{cov}[\Omega_i, \Omega_j]$, which reveals a correlation between the electron density distributions in basins Ω_i and Ω_j is analyzed. Going from the oxygen to tellurium atom one observes gradual decrease of the electron delocalization between the lone pairs of chalcogen: $V_1(X) \leftrightarrow V_2(X)$ and increase of delocalization between the lone pairs and core basin $V_1(X) \leftrightarrow C(X) \leftrightarrow V_2(X)$. In H_2O , H_2S and $H_2C=O$, $H_2C=S$ dominates an exchange between lone electron pairs: $\text{cov}[V_1(X), V_2(X)] > \text{cov}[V_{i=1,2}(X), C(X)]$, meanwhile for Se and Te containing molecules prevails a delocalization with core region: $\text{cov}[V_{i=1,2}(X), C(X)] > \text{cov}[V_1(X), V_2(X)]$. It is proposed that this effect is associated with not negligible penetration of d electrons from the outermost shell of the atomic core into valence shell. A study on the O_3 molecule reveals dominating delocalization between the lone pair $V(O)$ and electron density of the $O-O_{i=1,2}$ bonds: $V(O, O_{i=1}) \leftrightarrow V(O) \leftrightarrow V(O, O_{i=2})$, meanwhile an exchange between the chalcogen core $C(X)$ and lone pair $V(X)$: $C(X) \leftrightarrow V(X)$ prevails in SO_2 , SeO_2 and TeO_2 .

© 2007 Elsevier B.V. All rights reserved.

Keywords: Electron localisation function; *Ab initio* calculations; Selenium compounds; Sulphur compounds; Tellurium compounds; Chemical bond

1. Introduction

Since many decades understanding the nature of chemical bonds was one of the most important goals of chemistry. In recent years very powerful tool for theoretical analysis and interpretation of chemical bonds is an approach called generally as Quantum Chemical Topology (QCT) [1]. In the framework of QCT, which contain several

theoretical formalisms, two methods are especially popular among chemists: theory named as Atoms in Molecules (AIM) proposed by Bader [2] and topological analysis of Electron Localization Function (ELF) formulated by Silvi and Savin [3] on definition of ELF in formulation of Becke and Edgecombe [4]. Not going into details, the ELF is relative measure of electron localization associated with the spherically averaged conditional same-spin pair probability density and therefore is very interesting theoretical tool for study of nature of chemical bonds [5].

In the framework of the topological analysis of the electron density and Electron Localization Function (ELF) the quantum uncertainty of the basin population is measured

* Corresponding authors. Tel.: +48 713757440; fax: +48 713282348 (Z. Latajka).

E-mail addresses: sberski@wchuwr.chem.uni.wroc.pl (S. Berski), latajka@wchuwr.chem.uni.wroc.pl (Z. Latajka).

by the fluctuation (variance) in the mean number of electrons in a Ω -basin: $\sigma^2(\bar{N}, \Omega) = \langle N^2 \rangle_{\Omega} - \langle N \rangle_{\Omega}^2$ [6,7]. It has been proposed that it is a consequence of the electron delocalization. For a practical analysis of the electron delocalization the square of the standard deviation $\sigma^2(\bar{N}, \Omega)$ can be rewritten as $\sigma^2(\bar{N}, \Omega_i) = \sum_{j \neq i} (\bar{N}_i \bar{N}_j - \bar{N}_{ij}) = \sum_{j \neq i} \text{cov}(\Omega_i, \Omega_j)$ where the $\text{cov}(\Omega_i, \Omega_j)$ contributions are just a difference in the number of electron pairs between basins Ω_i and Ω_j expected in the limit of non-interacting basins and actual number of pairs. The pair covariance indicates how much of the population fluctuation of two given basins are correlated.

The electron density delocalization among ELF-basins has been already studied and for instance Llusar et al. [8] presented abnormally high values for the metal–metal covariance (0.124 (Pd) ÷ 1.371 (Tc)) as a main feature of the multiple metal–metal bonds in dimers of $M_2(\text{Formamidinate})_4$ with $M = \text{Nb}, \text{Mo}, \text{Tc}, \text{Ru}, \text{Rh}$ and Pd . Recently, Silvi [9] represented the electron density in molecules in terms of a superposition of promolecular densities or resonant Lewis structures on the basis of a correlation between the localization basins derived from the covariance matrix of the basin populations. Matito et al. [10] studied the electron fluctuation of the TS structure for a set of pericyclic and pseudopericyclic reactions observing accumulations of fluctuation for the pseudopericyclic ones. The survey of applications of electron localization function in description of electron delocalization has been reviewed by Poater et al. [11].

In this paper we present an analysis of bonding and electron delocalization in the H_2X , $\text{H}_2\text{C}=\text{X}$ and XO_2 ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) molecules by means of the covariance contributions to the electron density fluctuation calculated for ELF-basins. Furthermore, we discuss an effect of the basis set, focusing on role of the d orbitals of chalcogen. In the case of O_3 and SO_2 a difference in the chemical bonding is emphasized using different sets of mesomeric structures.

2. Computational details

Calculations have been performed within density functional methodology using the Gaussian 03 program [12] with the B3LYP electron density functional [13–15]. In the case of the H_2X and $\text{H}_2\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}$) molecules three types of the basis sets have been adopted: (1) 6-311++G(3d,3p) (TZVP), (2) 6-311++G(3df,3pd) (TZVP1), both as included in the G03 program, (3) the ‘DZVP (DFT Orbital)’ basis set proposed by Godbout et al. [16,17] (DZVP). For XO_2 ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) the basis sets used are: (1) 6-311G(d,p) (TZVP), (2) 6-311++G(3df,3pd) (TZVP1), both as included in the G03 program, (3) ‘DZVP (DFT Orbital)’ (DZVP) [16]. We decided to use the DZVP basis set for Te in order to have a comparison with other molecules. Additional calculations for TeO_2 have been carried out using the small-core relativistic pseudopotential PP (Te) with the aug-cc-pVTZ-PP (Te) [18] and aug-cc-pVTZ (O) [19,20] basis sets.

A topological analysis of the ELF function has been performed by means of the TopMod suit [21]. The ELF function has been calculated over a rectangular parallelepipedic grid with the step $\Delta r < 0.1$ bohr.

3. Results and discussion

3.1. The H_2X and $\text{H}_2\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) molecules

The basin populations (\bar{N}) computed for the $\text{H}_2\text{C}=\text{X}$ and H_2X molecules are collected in Tables 1 and 2, respectively. In both molecules core electrons are described by the core basins: C(C), C(X) and the $\text{C}-\text{H}_{i=1,2}$ bonds by disynaptic protonated basins $\text{V}(\text{H}_{i=1,2}, \text{C})$. The lone electron pairs of chalcogen X are reflected by non-bonding basins $\text{V}_1(\text{X})$ and $\text{V}_2(\text{X})$ which in $\text{H}_2\text{C}=\text{X}$ are localized on the σ_v symmetry plane and are coplanar with the $\text{C}-\text{H}_{i=1,2}$ bonds. A description of the carbon–chalcogen bond $\text{C}=\text{X}$ which is formally of the double type depends on the basis set adopted for the computations. Using the DZVP basis set there are localised two bonding $\text{V}_{i=1,2}(\text{C}, \text{X})$ basins ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}$) lying below and above the symmetry plane. Calculations with the 6-311++G(3d,3p) basis set (TZVP) yields only one $\text{V}(\text{C}, \text{X})$ basin for $\text{H}_2\text{C}=\text{O}$, $\text{H}_2\text{C}=\text{S}$ (Fig. 1) and a pair of basins $\text{V}_{i=1,2}(\text{C}, \text{Se})$ for $\text{H}_2\text{C}=\text{Se}$. Since the importance of f-type polarization functions for correct *ab initio* and DFT calculations of sulphur compounds has been previously established [22] calculations with the largest basis set 6-311++G(3df,3pd) (TZVP1) are included here. An expected effect is really evidenced and one observes a pair of $\text{V}_{i=1,2}(\text{C}, \text{X})$ attractors for $\text{X} = \text{S}, \text{Se}$ and single attractor $\text{V}(\text{C}, \text{O})$ for $\text{H}_2\text{C}=\text{O}$. The basis set dependence may be explained by very flat ELF-surface between the $\text{V}_{i=1,2}(\text{C}, \text{X})$ attractors since a difference between ELF-values for $\text{V}_{i=1,2}(\text{C}, \text{X})$ attractors and (3, –1) critical point associated with a splitting of the $\text{V}_{i=1,2}(\text{C}, \text{X})$ basin into isolated $\text{V}_1(\text{C}, \text{X})$ and $\text{V}_2(\text{C}, \text{X})$ basins equals (DZVP) 0.001 (S) and 0.005 (Se).

The basin populations (\bar{N}) calculated for the $\text{H}_2\text{C}=\text{X}$ and H_2X molecules are collected in Tables 1 and 2, respectively. A population of the $\text{C}=\text{X}$ bond (DZVP), possessing clear covalent character, ranges between 2.44e ($\text{H}_2\text{C}=\text{O}$) and 2.73e ($\text{H}_2\text{C}=\text{Te}$) and an amount of the electron density increases going down 16 group of the periodic table. The formal bond order ($\approx 1.2 \div 1.3$) is smaller than corresponding to the double type $\text{C}=\text{X}$ bond (2.0). A difference between the $\text{V}(\text{C}, \text{S})$ and $\text{V}(\text{C}, \text{Se})$ basins of 0.04e (DZVP) is reduced to about 0.01e using larger basis set (TZVP) what corresponds to similar electronegativities of S and Se. A saturation of the basis set with f-type functions (TZVP1) leads to an increase of the basin population of $\text{V}(\text{C}, \text{S})$ in comparison to TZVP by about 0.1e. In the case of H_2X the basin population (DZVP) of the $\text{H}_{i=1,2}-\text{X}$ bonds gradually increases from 1.58e (H_2O) to 1.86e (H_2Se) thus atoms share an electron with each other and form bonds with increasing covalent character (see Table 2).

Download English Version:

<https://daneshyari.com/en/article/1411812>

Download Persian Version:

<https://daneshyari.com/article/1411812>

[Daneshyari.com](https://daneshyari.com)