



Intramolecular C—S···O=S(C) chalcogen bonds: A theoretical study of the effects of substituents and intermolecular hydrogen bonds



Yanhua Wang^a, Yuchen Zhang^b, Zhijian Xu^c, Jianying Tong^a, Wei Teng^a, Yunxiang Lu^{b,*}

^a College of Biology and Environment Engineering, Zhejiang Shuren University, Hangzhou 310015, China

^b Key Laboratory for Advanced Materials and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China

^c Drug Discovery and Design Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

ARTICLE INFO

Article history:

Received 23 May 2017

Received in revised form 25 June 2017

Accepted 26 June 2017

Available online 27 June 2017

Keywords:

Intramolecular chalcogen bonds

M06-2x

CSD

Intermolecular hydrogen bonds

ABSTRACT

According to our search of the Cambridge Structural Database, a huge number of crystal structures involving intramolecular C—S···O=S(C) interactions were extracted. The largest proportion of these interactions in the crystals shows rather good linearity and short interatomic S···O distances. Then, intramolecular C—S···O=S(C) interactions in three representative organic molecules, i.e. sulfamethizole, thioindirubin, and thiazolo-pyridinium methide, were investigated using density functional theory calculations at the M06-2x level. The effects of different substituents and intermolecular hydrogen bonds on these interactions were also examined. The presence of both electron-withdrawing and electron-donating substituents into the donor moiety tends to strengthen intramolecular S···O bonds, while the formation of intermolecular hydrogen bonds has a complex influence. To gain a deeper understanding of the nature and strength of these interactions, the analyses of atom in molecules, noncovalent interaction index, and natural bond orbital were undertaken. Intramolecular chalcogen bonds are weak electrostatic interactions and play a key role in controlling the crystal forms of relevant organic compounds, frequently supported by intermolecular hydrogen bonds.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The study of specific noncovalent interactions, such as halogen bonding, chalcogen bonding, pnictogen bonding, and tetrel bonding, has become a hot topic in structural chemistry, due to their fundamental importance in crystal packing and supramolecular assembly [1–4]. These interactions have been termed as σ -hole interactions by Murray et al. [5,6], because covalently-bonded Group IV–VII atoms exhibit the regions of positive electrostatic potential on the extension of covalent bonds to these atoms. Negative centers, such as lone pairs of Lewis bases, anions, π electrons, etc., tend to approach the positive σ -hole, thereby giving rise to directional noncovalent interactions. These σ -hole interactions show some similar properties: the interactions become gradually stronger along with the increase of the size of the donor atoms; the attachment of electron-attracting groups to the donor atoms produce stronger interactions.

In recent years, intramolecular interactions involving divalent sulfur, e.g. S···O and S···N contacts, have been found to be significant in the molecular conformations of a large number of organic

compounds [7–10]. In 2010 Shishkin and co-workers revealed that molecular conformation of thioindirubin (an indigoid dye) creates suitable conditions for the formation of intramolecular C—S···O=C interactions via X-ray diffraction and quantum chemical calculations [7]. Subsequently, the conformational features of acetazolamide (a diuretic drug) were analyzed by Nagao et al., and they detected that intramolecular C—S···O=S interaction could regulate the molecular conformation even in the complex structures with enzymes [8]. Very recently, intramolecular C—S···O=S chalcogen bonding and its potential to lock molecular conformation were examined in the crystal forms of sulfamethizole (a sulfonamide antibiotic) using experimental electron density analysis and crystallographic refinement technique [9].

According to our survey of the Cambridge Structural Database (CSD) [11], a huge number of crystal structures containing intramolecular C—S···O=S(C) bonds were retrieved. Considering the important role of these interactions in controlling the molecular conformations of quite a few organic compounds, it is of great importance to characterize the nature and strength of intramolecular chalcogen bonding from a theoretical point of view.

In the present work, intramolecular S···O interactions in three representative organic molecules, i.e. sulfamethizole, thioindirubin, and thiazolo-pyridinium methide (Fig. 1), were studied in

* Corresponding author.

E-mail address: yxlu@ecust.edu.cn (Y. Lu).

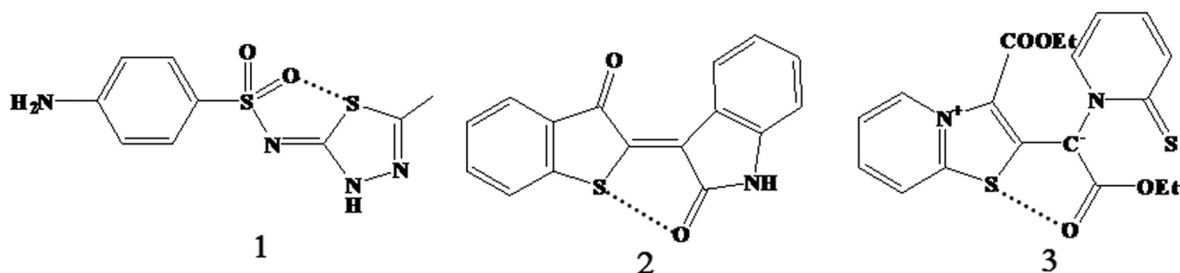


Fig. 1. Chemical structures of the compounds 1–3.

detail using density functional theory (DFT) calculations at the M06-2x level. Sulfamethizole (**1**) is a sulfanamide antibiotic known to inhibit the bacterial dihydropteroate synthetase [9], and thioindirubin (**2**) belongs to the famous class of indigoid dyes [7]. The molecule **3** is a mesoionic compound showing a short S \cdots O distance in the crystal structure (about 2.5 Å) [12]. To explore the substituent effects on these interactions, two electron-withdrawing substituents (CF₃, CN) and two electron-donating substituents (OCH₃, NH₂) were introduced into the C–S moiety in the five-membered ring of the molecule **1**. Particularly, the influence of the formation of intermolecular hydrogen bonds was also investigated herein, because intermolecular hydrogen bonds always take place in the crystal structures of **1** and **2** [7,9]. As shown in Fig. 2, two kinds of intermolecular hydrogen bonds were considered for the molecule **1**: the N–H group in the five-membered ring establishes hydrogen bonds with halide anions (N–H \cdots X[−]); the ring N atom forms hydrogen bonds with hydrogen halide (N \cdots H–X). For the molecule **2**, intermolecular hydrogen bonds between the proton attached to the ring N and halide anions were taken into account, somewhat similar to that in the compound **1**. This is the first theoretical study to examine the influence of intermolecular hydrogen bonds on intramolecular chalcogen bonds that usually occur in the crystals. In addition, in order to gain a deeper understand of the characteristics of these interactions, the atoms in molecules (AIM), noncovalent interaction index (NCI), and natural bond orbital (NBO) analyses were presented.

2. Computational methods

All the calculations in this work were carried out with the Gaussian 09 suite of programs [13]. The geometries of all the molecules

under study were fully optimized by means of the DFT/M06-2X method [14], which has been commonly applied to study various types of noncovalent interactions [15,16]. Two Dunning's basis sets, aug-cc-pVDZ and aug-cc-pVTZ, were used for all atoms [17,18]. The topological analysis of the molecules under study was carried out with the help of AIM 2000 software [19], using the wave functions generated at the level of M06-2X/aug-cc-pVDZ. The NCI analysis and the NBO plots were done with the Multiwfn program [20] and visualized using the VMD package [21].

3. Results and discussion

3.1. CSD survey

The CSD is a convenient and reliable storehouse for structural information. It is very useful to find structural information of non-covalent interactions from high-resolution structures of small molecules deposited in the CSD. To obtain structural features of intramolecular S \cdots O chalcogen bonds in crystal structures, a search of the CSD (version 5.36, updates November 2014) was performed using the following criteria: (1) the S \cdots O distances are in the range of 2.24–3.44 Å, less than the sum of the van der Waals (vdW) radii of the S and O atoms [22]; (2) the C–S \cdots O angles are larger than 150°; (3) the (C)S=O \cdots S angles vary from 90° to 120° as those observed in the reported crystals [7–10]. According to our search of the CSD, 1586 crystal structures involving intramolecular C–S \cdots O=S(C) bonds were extracted, which indicates the rather ubiquitous occurrence of such intramolecular interactions in the crystals.

The dependencies between the numbers of intramolecular S \cdots O interactions extracted from the CSD and two structural parameters,

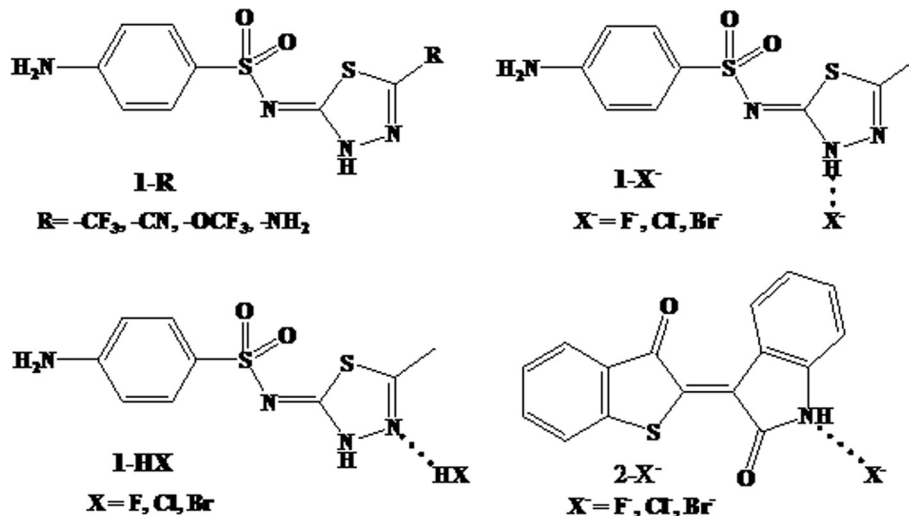


Fig. 2. Chemical structures of the systems under study.

Download English Version:

<https://daneshyari.com/en/article/5392329>

Download Persian Version:

<https://daneshyari.com/article/5392329>

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