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IUPAC Recommendations

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Definition of the chalcogen bond (IUPAC Recommendations 2019)

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Abstract: This recommendation proposes a definition for the term “chalcogen bond”; it is recommended the term is used to designate the specific subset of inter- and intramolecular interactions formed by chalcogen atoms wherein the Group 16 element is the electrophilic site.

Keywords: chalcogen bond; IUPAC Organic and Biomolecular Chemistry Division; IUPAC Physical and Biophysical Chemistry Division; nomenclature; noncovalent interactions; self-assembly; supramolecular chemistry.

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1 Preface

This recommendation proposes a definition for the term “chalcogen bond” and suggests it be used to designate a subset of the inter- and intramolecular interactions formed by chalcogen atoms (*i.e.* atoms of Group 16 elements, see p. 51 in [1]) in a molecular entity (see p. 1142 in [2]).

Oxygen, the chalcogen with highest electronegativity and lowest polarizability, frequently functions as a nucleophile. Other elements of Group 16 can behave similarly, *e.g.* when working as hydrogen bond [3] or halogen bond [4] acceptors. When doing so, chalcogen atoms behave as electron-rich (nucleophilic) (see p. 1111 in [2]) sites and form net attractive interactions with electron-poor (electrophilic) partners (see p. 1146 in [2]). Chalcogen atoms can also function as electron-poor (electrophilic) sites, *i.e.* they can attractively interact with electron-rich (nucleophilic) sites. Interactions in the two cases described above differ in their electronic features and several other characteristics, *e.g.* their directionality relative to the covalent bonds formed by the chalcogen atom. *It is recommended that the term “chalcogen bond” is used uniquely to designate the latter set of noncovalent interactions described above.*

The chalcogen bond definition given in this paper adopts the same mindset as other terminologies, where interactions are named by referring to the electrophilic site. Specifically, it is consistent with:

- the IUPAC definitions of the hydrogen bond [3] and halogen bond [4], where the hydrogen and halogen atoms are the electrophiles;
- the terms “pnictogen bond (PnB)” and “tetrel bond (TtB)”, which are increasingly used in the literature to designate attractive interactions formed by elements of Groups 15 and 14 of the Periodic Table in the solid, liquid, and gas phases when the respective elements act as the electrophilic site [5].

The term defined by this recommendation and the related terms mentioned above thus constitute parts of a comprehensive terminology for interactions where the presence of an electrophilic and a nucleophilic site can be unequivocally identified *via* experimental and/or theoretical features. This terminology offers the advantage of being systematic (it is based on the Groups of the Periodic Table), unambiguous (similar to the hydrogen and halogen bonds definitions and to other terms referring to the Group of the Periodic Table to which the electrophilic site belongs), and descriptive (it inherently conveys information on some key features of the respective interactions, *e.g.* their polar character and geometric preferences).

A short definition of the term is given first, followed by explanatory examples in the form of a not exhaustive list of common chalcogen bond donors and acceptors. This recommendation is concluded by a list of experimental and/or theoretical features, which, although not comprehensive, can be used as evidence for the presence of a chalcogen bond.

2 Definition

chalcogen bond (ChB)

net attractive interaction between an *electrophilic* region associated with a *chalcogen* atom in a *molecular entity* and a *nucleophilic* region in another, or the same, molecular entity.

Note 1: A typical chalcogen bond is denoted by the three dots in R–Ch···A, where Ch is the ChB donor, being any chalcogen atom (possibly hypervalent) having an electrophilic (electron-poor) region, R is the remainder of the molecular entity R–Ch containing the ChB donor, and A is the ChB acceptor and is typically a molecular entity possessing at least one nucleophilic (electron-rich) region.

Note 2: Chalcogen atoms can concurrently form one or more than one chalcogen bond.

Note 3: Chalcogen atoms of a molecular entity give rise to a variety of interactions with different electronic and geometric features. The term chalcogen bond must not be used for interactions where the chalcogen (frequently oxygen) functions as a nucleophile. The attractive intermolecular interaction between the oxygen

atoms of an alcohol or a carboxylic acid and the acidic proton of another alcohol or carboxylic acid molecule is not a chalcogen bond, it is a hydrogen bond; the attractive intermolecular interaction between 1,4-dithiane and iodine atoms of diiodine or triiodomethane is not a chalcogen bond, it is a halogen bond; the attractive intermolecular interaction between bismuth and selenium atoms of tris(selenophen-2-yl)-bismuthane is not a chalcogen bond, it is a pnictogen bond (PnB); and the attractive intramolecular interactions between tin and sulphur atoms in crystalline 2,10-dichloro-2,10-dimethyl-2,10-distanna-6-thiaundecane is not a chalcogen bond, it is a tetrel bond (TtB).

2.1 List of some common chalcogen bond donors and acceptors

Some common ChB donors and acceptors are itemized below.

The molecular entity R–Ch can be a:

- five membered and chalcogen containing heterocycle:
 - a thio-, seleno-, and tellurophene derivative and a fused polycyclic derivative thereof
 - a chalcogen-containing azole and a fused polycyclic derivative thereof (*e.g.* selenazoles, tellurazoles, thiadiazoles, their benzo-fused derivatives)
 - a chalcogen-containing azolium cation and a fused polycyclic derivative thereof (*e.g.* thiazolium, isothiazolium, selenazolium, cations and their benzo-fused analogues)
 - an *N*-oxide of a chalcogen-containing azole and a fused polycyclic derivative thereof (*e.g.* furoxans, 2,5-thiadiazoles *N*-oxides, tellurazoles *N*-oxides)
- thio-, seleno-, and telluroanhydride and an analogue where sulfonyl group(s) substitute for carbonyl(s) (*e.g.* telluraphthalic anhydride, Beaucage reagent)
- thio-, seleno-, and tellurocyanate (*e.g.* sulfane dicarbonitrile, phenylselenocyanate, benzyl tellurocyanate)
- sulfoxide and selenoxide (*e.g.* dimethylsulfoxide, dimethylselenoxide)
- λ^4 chalcogen compound and particularly a polyhalo-, polyoxa-, and polyaza λ^4 chalcogen derivative (*e.g.* SF₄, Martin sulfurane reagent, ozone)

The ChB acceptor A can be a:

- lone pair possessing atom (*e.g.* N atom of a pyridine or an amine, O atom of an ether or a carbonyl group)
- π system (*e.g.* double or triple bond, arene moiety)
- anion (*e.g.* halide anion, polyatomic oxyanion)

2.2 List of features

The evidence for the occurrence of a ChB may be experimental or theoretical, or better, a combination of both. Some features that are useful as indications for the ChB, are included in a list below, which is not necessarily exhaustive. The greater the number of features satisfied, the more reliable the characterization of an interaction as a ChB.

In a typical chalcogen-bonded complex R–Ch \cdots A:

- the interatomic distance between the ChB donor atom Ch and the nucleophilic site in the acceptor A tends to be less than the sum of the van der Waals radii and more than the sum of covalent radii
- the ChB acceptor A tends to approach the donor atom Ch on the side of the atom along the extension of one of the σ covalent bonds at Ch and opposite to the bond; deviation from the extension is frequently more pronounced in ChBs than in halogen bonds [6]
- when the nucleophilic moiety is a lone pair orbital, or a π region, of the acceptor A, the ChB donor Ch tends to approach A along the axis of the lone pair, or perpendicular to the π bond plane, respectively
- the R–Ch covalent bond opposite to the ChB is usually longer in the chalcogen-bonded adduct than in the unbonded ChB donor

- with a given acceptor A, the ChB strength typically decreases as the electronegativity of Ch increases, and the electron withdrawing ability of R decreases
- the analysis of the electron density topology usually shows a bond path and a bond critical point between Ch and A (see pp. 1927 and 1928, respectively, in [7])
- the infrared absorption and Raman scattering observables of both R–Ch and A are affected by ChB formation; new vibrational modes associated with the formation of the Ch ··· A bond are also characteristically observed
- the UV–vis absorption bands of the ChB donor chromophore usually shift to longer wavelengths upon ChB formation
- the Ch ··· A ChB formation typically affects the nuclear magnetic resonance observables (e.g. chemical shift values) of nuclei in both R–Ch and A.

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