

Definition of the halogen bond (IUPAC Recommendations 2013)*

Gautam R. Desiraju¹, P. Shing Ho², Lars Kloo³, Anthony C. Legon⁴,
Roberto Marquardt⁵, Pierangelo Metrangolo^{6,‡}, Peter Politzer⁷,
Giuseppe Resnati^{6,‡}, and Kari Rissanen⁸

¹Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India; ²Department of Biochemistry and Molecular Biology, Colorado State University, Fort Collins, CO 80523-1870, USA; ³Department of Chemistry, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden; ⁴School of Chemistry, University of Bristol, Bristol BS8 1TS, UK; ⁵Laboratoire de Chimie Quantique, Institut de Chimie, Université de Strasbourg, 4, rue Blaise Pascal - CS90032, 67081 Strasbourg, France; ⁶Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Milano 20131, Italy; ⁷CleveTheoComp, 1951 W. 26th Street, Suite 409, Cleveland, OH 44113, USA; ⁸Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014 JYU, Finland

Abstract: This recommendation proposes a definition for the term “halogen bond”, which designates a specific subset of the inter- and intramolecular interactions involving a halogen atom in a molecular entity.

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

1. PREAMBLE

This recommendation proposes a definition for the term “halogen bond”, which designates a specific subset of the inter- and intramolecular interactions involving a halogen atom in a molecular entity. (A “molecular entity” is defined as “Any constitutionally or isotopically distinct atom, molecule, ion, ion pair, radical, radical ion, complex, conformer etc., identifiable as a separately distinguishable entity”, see p. 1142 in ref. [1]). Consistent with their relatively high electronegativity, halogen atoms can behave as electron-rich (nucleophilic) sites and form net attractive interactions with electron-poor (electrophilic) partners. A halogen atom functioning as hydrogen bond acceptor is a typical example of such interactions. Halogen atoms can also function as electron-poor (electrophilic) sites and attractively interact with electron-rich (nucleophilic) sites. The two sets of interactions differ for their electronic features and several other characteristics, e.g., their directionality relative to the covalent bond(s) formed by the halogen atom. The term “halogen bond” identifies the latter set of noncovalent interactions described above. After a short definition of the term, a list (not exhaustive) of common halogen bond donors and acceptors is given. A list of experimental and/or theoretical features, which, although

*Sponsoring body: IUPAC Physical and Biophysical Chemistry Division: see more details on p. 1713.

‡Corresponding authors: E-mail: P.M.: pierangelo.metrangolo@polimi.it; G.R.: giuseppe.resnati@polimi.it

not exhaustive, can be used as evidence for the presence of a halogen bond concludes this recommendation.

A comprehensive technical report, to be published, has been prepared by the task group in order to relate the proposed definition with the past work on halogen bond and provide the rationale for the proposed definition.

2. DEFINITION

A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity [1].

A typical halogen bond is denoted by the three dots in $R-X\cdots Y$. $R-X$ is the halogen bond donor, X is any halogen atom with an electrophilic (electron-poor) region, and R is a group (see p. 1118 in ref. [1]) covalently bound to X . In some cases, X may be covalently bound to more than one group (see p. 1118 in ref. [1]). It may also form more than one halogen bond. Y is the halogen bond acceptor and is typically a molecular entity (see p. 1142 in ref. [1]) possessing at least one nucleophilic (electron-rich) region. Some common halogen bond donors and acceptors are itemized below.

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

2.1 List of some common halogen bond donors and acceptors

$R-X$ can typically be a:	dihalogen molecule (e.g., I_2 , Br_2 , ICl , ClF) haloalkane (e.g., CBr_4 , CHI_3 , $C_nF_{2n+1}I$) haloarene or haloheteroarene (e.g., iodobenzene, halopyridinium and haloimidazolium cations) 1-haloalkyne (e.g., diiodoacetylene) halonium ion (e.g., diphenyliodonium or bromonium derivatives) haloimide (e.g., <i>N</i> -bromo- or <i>N</i> -iodosuccinimide)
Y can typically be a:	lone pair possessing atom (e.g., N atom of a pyridine or an amine, O atom of a carbonyl group) π system (e.g., double or triple bonds, arene moiety) anion (e.g., halide anion, oxyanion)

2.2 List of features

In a typical halogen-bonded complex $R-X\cdots Y$:

- The interatomic distance between X and the appropriate nucleophilic atom of Y tends to be less than the sum of the van der Waals radii.
- The length of the $R-X$ covalent bond usually increases relative to the unbonded $R-X$.
- The angle $R-X\cdots Y$ tends to be close to 180° , i.e., the halogen bond acceptor Y approaches X along the extension of the $R-X$ bond.
- The halogen bond strength decreases as the electronegativity of X increases, and the electron-withdrawing ability of R decreases.
- The forces involved in the formation of the halogen bond are primarily electrostatic, but polarization, charge transfer, and dispersion contributions all play an important role. The relative roles of the different forces may vary from one case to the other.

- The analysis of the electron density topology usually shows a bond path (a “bond path” and a “bond critical point” are defined as “Within the *topological electron distribution theory*, the line resulting from the addition of two gradient paths of the *electron density function* emanating from the *bond critical point* located between each two neighbouring atomic basins” and “Within the *topological electron distribution theory*, a (3, -1) critical point (the point of the gradient field of the electron density within a given neutral configuration in which $\nabla\rho(r,q) = 0$) which is a local maximum in two directions and is a local minimum in the third, i.e. a *saddle point* in the three directions”, see pp. 1928 and 1927, respectively, in ref. [2]) connecting X and Y and a bond critical point (see pp. 1928 and 1927, respectively, in ref. [2]) between X and Y.
- The infrared absorption and Raman scattering observables of both R–X and Y are affected by halogen bond formation; new vibrational modes associated with the formation of the X···Y bond are also observed.
- The UV–vis absorption bands of the halogen bond donor usually shift to shorter wavelengths.
- The X···Y halogen bond usually affects the nuclear magnetic resonance (NMR) observables (e.g., chemical shift values) of nuclei in both R–X and Y, both in solution and in the solid state.
- The binding energies of the peaks associated with X with the X-ray photoelectron spectrum (XPS) of the complex shift to lower energies relative to unbonded X.

MEMBERSHIP OF SPONSORING BODY

Membership of the IUPAC Physical and Biophysical Chemistry Division Committee for the period 2012–2013 is as follows:

President: K. Yamanouchi (Japan); **Vice President:** R. Marquardt (France); **Secretary:** A. Wilson (USA); **Past President:** A. McQuillan (New Zealand); **Titular Members:** K. Bartik (Belgium); A. Friedler (Israel); A. Goodwin (USA); R. Guidelli (Italy); A. Russell (UK); J. Stohner (Switzerland); **Associate Members:** V. Barone (Italy); A. Császár (Hungary); V. Kukushkin (Russia); V. Mišković-Stanković (Serbia); Á. Mombrú Rodríguez (Uruguay); X. S. Zhao (China); **National Representatives:** K. Bhattacharyya (India); J. Cejka (Czech Republic); S. Hannongbua (Thailand); M. Koper (Netherlands); A. J. Mahmood (Bangladesh); O. Mamchenko (Ukraine); J. Mdoe (Tanzania); F. Quina (Brazil); N. Soon (Malaysia); V. Tomišić (Croatia).

This document was prepared in the frame of IUPAC Project #2009-032-1-100, Categorizing Halogen Bonding and Other Noncovalent Interactions Involving Halogen Atoms. **Chairs:** P. Metrangolo and G. Resnati; **Members:** G. R. Desiraju; P. Ho; L. Kloo; A. Legon; R. Marquardt; P. Politzer; K. Rissanen.

See the following web site for more details: <http://www.halogenbonding.eu>.

REFERENCES

1. P. Muller. *Pure Appl. Chem.* **66**, 1077 (1994).
2. V. I. Minkin. *Pure Appl. Chem.* **71**, 1919 (1999).

Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.