

# What's in a name? Noncovalent $\text{Ar}-\text{Cl}\cdots(\text{H}-\text{Ar}')_n$ interactions and terminology based on structure and nature of the bonding†

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Interactions are named based on the interacting moieties and on the mechanism of their interaction. These approaches are independent. The former approach relies on the knowledge of structure alone and the latter requires additional knowledge about electronic structure. Knowledge about the nature of the bonding is additional knowledge; it serves to provide detail and this knowledge should not be used to exclude the naming of the interaction based on structure alone.

In our recent communication on “Multifurcated halogen bonding involving  $\text{Ph}-\text{Cl}\cdots\text{H}-\text{CPh}=\text{N}-\text{R}'$  interactions and its relation to idioteloamphiphile layer architecture”, we discussed the role of halogen bonding in the crystal structure of 4-chlorobenzaldazine.<sup>1</sup> The study is one part of a program that aims at the creation of polar order by rational design.<sup>2–4</sup> Our use of the term “halogen bonding” in this communication is different from the use by Metrangolo *et al.*,<sup>5</sup> this difference was noted by Metrangolo, Pilati, and Resnati (MPR), and this recognition has led to their comment entitled “Halogen bonding and other noncovalent interactions involving halogens: a terminology issue”.<sup>6</sup>

MPR write that the term *halogen bonding* (abbreviated as XB) should be used *exclusively* for the description of “any noncovalent interaction involving halogens as acceptors of electron density” and MPR exemplify with the general scheme  $\text{D}\cdots\text{X}-\text{Y}$ , where X is the halogen (Lewis acid, XB-donor), D is any electron-donor (Lewis base, XB-acceptor), and Y is carbon, halogen, nitrogen, *etc.* MPR note similarities of this definition of halogen bonding with the usage of the term hydrogen bonding (HB) for the description of noncovalent interaction of the type  $\text{D}\cdots\text{H}-\text{Y}$ , where D is an electron-donor (HB-acceptor) and H–Y is the hydrogen bond donor.

The word “interaction” signifies a “mutual or reciprocal action or influence” and in the present context the influence is “attraction” or “affinity”. One way to name a bonding interaction is to name the partners involved in the interaction. It takes at least two partners to engage in bonding and the terminology is easily applied if only two partners are involved: carbon–carbon bonding in alkanes, carbon–chlorine bonding in alkyl halides, lithium–carbon bonding in organolithiums and so on. The same approach can be applied to intermolecular interactions and this is exemplified by terms like ammonia–borane bonding or arene–arene bonding. This terminology relies entirely on the naming of the interacting

moieties and, in particular, it is *independent* of the nature of the interaction. This terminology is applied to covalent bonds (C–C), ionic bonds ( $\text{Li}^+\text{F}^-$ ,  $\text{Li}^+\text{R}^-$ ), coordination bonds (also known as dative bonds,  $\text{H}_3\text{N} \rightarrow \text{BH}_3$ ), hydrogen bonds ( $\text{HOH}\cdots\text{OH}_2$ ), and a variety of non-covalent bonding situations (electrostatic, dispersion).

The naming is easily accomplished for any interaction that involves two bonding partners, A and B; A interacts with B, B interacts with A, A and B interact with each other, and the result is AB bonding. This naming becomes more involved when one moiety A is bonded to a number *n* of moieties B and “additivity” is the first approximation for the bonding and the nomenclature. This is taken for granted in organic chemistry;  $\text{CH}_2$  forms two carbon–carbon bonds with the two  $\text{CH}_3$  groups in propane and all the non-additive components of the overall interaction between the methylene and the methyl groups appear in the terminology of conformational theory. Additivity is also the basis for the naming of interactions in complexes;  $\text{Li}^+$  is solvated by four ether molecules and there are four lithium cation–ether bonds. The overall interaction of  $\text{Li}^+(\text{OR}_2)_4$  also includes ligand–ligand interactions and this is neglected in the terminology. Such neglect is benign, done with good reason and in a systematic manner, and doing so brings into focus the leading term of the overall interaction. One systematic simplification in nomenclature serves to emphasize one bonding partner over the other. The term lithium ion solvation is used, for example, because it is short and because the solvent shell of  $\text{Li}^+(\text{OR}_2)_n$  is not really all that well known. The term lithium ion solvation is, in fact, more precise because it does not imply knowledge that does not really exist. Analogous considerations apply to clusters and they apply *independently* of the nature of the interactions. Examples might include benzene hydration in aggregates  $\text{C}_6\text{H}_6\cdot(\text{OH}_2)_n$ , or benzene solvation in methane aggregates  $\text{C}_6\text{H}_6\cdot(\text{CH}_4)_n$ . This kind of simplification is sensible only if the abbreviated terminology names the unique bonding partner.

It is an entirely different matter to characterize the mechanism of bonding. The characterization of the nature of the bonding requires not only knowledge of structure (the geometry of the nuclei) but also knowledge of the electronic structure (the geometry of the nuclei and of the electrons). In

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**Table 1** Pair binding energies

Molecule or pair	Total energy/atomic units			Binding energy/kcal mol <sup>-1</sup>		
	RHF	B3LYP	MP2(full)	RHF	B3LYP	MP2(full)
Azine	-1563.845180	-1569.432641	-1566.741528			
Intralayer Pair Orange	-3127.690044	-3138.865274	-3133.498383	-0.20	-0.00	9.62
Intralayer Pair Green	-3127.691569	-3138.866501	-3133.495519	0.76	0.76	7.82
Interlayer Pair Blue	-3127.689806	-3138.864887	-3133.485968	-0.35	-0.25	1.83
Interlayer Pair Red	-3127.689673	-3138.864587	-3133.484810	-0.43	-0.44	1.10

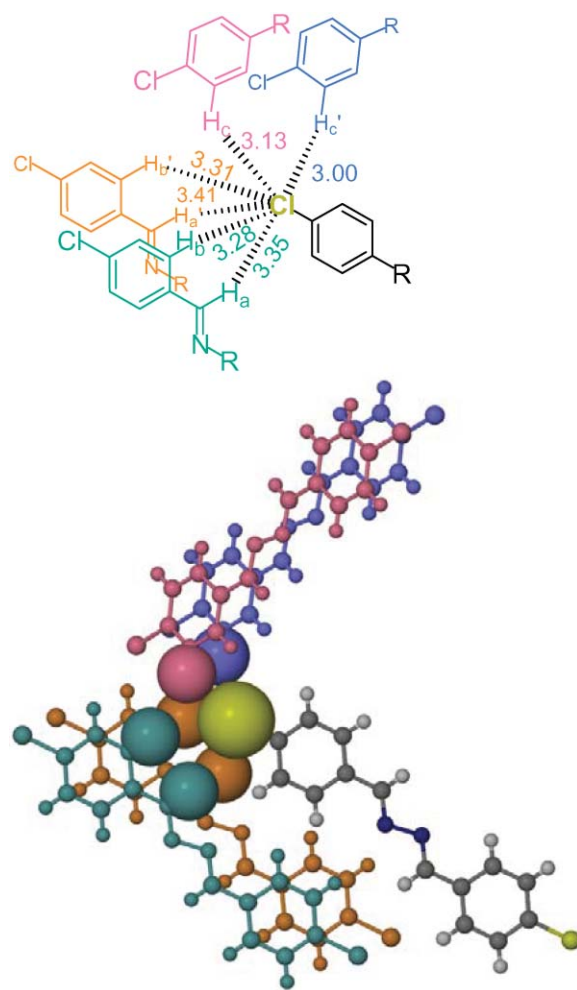
some cases knowledge about the nature of the bonding is well-established and the interaction can be characterized *via* its bonding partners (carbon-carbon bonding), the nature of their bonding (covalent bonding), or both (covalent carbon-carbon bonding). In other cases the establishment of the nature of the bonding requires years of research and debate, *i.e.* dative bonding,<sup>7</sup> back-dative bonding.<sup>8,9</sup> In many cases the nature of the bonding is merely assumed but not established.

The term *hydrogen bonding* started out with precise meaning, namely the interaction between two overall neutral molecules with each containing a polar X-H or Y-H bond and X and Y being undisputed electronegative atoms (O, N).<sup>10</sup> Water dimer is the quintessential model of hydrogen bonding; H-(H)O...H-OH. The leading term of the H-Y...H-X interaction is the dipole-dipole attraction associated with the bond dipole moments  $\mu(\text{H-Y})$  and  $\mu(\text{H-X})$ .<sup>11</sup> The usage of the term *hydrogen bonding* has drastically changed over the past two decades and this change has occurred particularly in the solid state community. To invoke hydrogen bonding it is no longer necessary that the HB acceptor Y has an H-atom attached, that the acceptor Y is the negative pole of a bond dipole, that the HB donor's H-atom H(X) is attached to an undisputed electronegative element (X = O, N), that the H-atom of the HB donor (HX) is the positive pole of a bond dipole, or even that the overall system is neutral. Clearly, the usage of hydrogen bonding in terms of geometry has become less restrictive, more inclusive, and its usage may now include essentially any hydrogen bridging situation Y...H-X with an H-atom between a great variety of X and Y.<sup>12</sup> Consequently, the mechanism of such hydrogen bonding has also expanded and it might now involve a variety of leading terms that cover a wide range of interaction energies from charge-dipole interactions all the way to nothing but dispersion.<sup>13</sup>

In the crystal structure of 4-chlorobenzaldazine the chlorine atom of a chlorobenzene moiety is positioned in a pocket formed by H<sub>a</sub>-atoms attached to azine-carbons C<sub>az</sub> and aromatic H<sub>b</sub>- and H<sub>c</sub>-atoms of chlorobenzene moieties of neighboring azines (Fig. 1). One can refer to the resulting Ar-Cl...(H-Ar')<sub>n</sub> intermolecular interaction as Ar-Cl...(H-Ar')<sub>n</sub> hydrogen bonding in the modern sense, *i.e.* the mere presence of hydrogen bridges, and so long as it is understood that nothing is implied about the nature of the bonding. In analogy to solvation terminology, we adopted the perspective where chlorine is taken to be the central bonding partner engaged (in intramolecular bonding with its azine, of course, and) in intermolecular bonding with several "ligands" H-Ar; thus the term Ar-Cl...(H-Ar')<sub>n</sub> *halogen bonding*. It is one advantage of this approach that no unwarranted implications are made as to

the precise number of H-Ar' neighbors that actually are in *attractive* interactions.

MPR note that interactions involving C(sp<sup>2</sup>)-attached H-atoms and halogens (F, I) in the structures of halobenzaldazines have been referred to as hydrogen bonding<sup>14,15</sup> and they present this information "as a confirmation of this terminology misuse". We see no conflict whatsoever with the preference of the authors of ref. 14 and 15 for the term hydrogen bonding over the use of halogen bonding; we consider both terms equally appropriate. MPR's use of the term hydrogen bonding in those cases implies that they have no problem with the recent, more expanded usage of the term

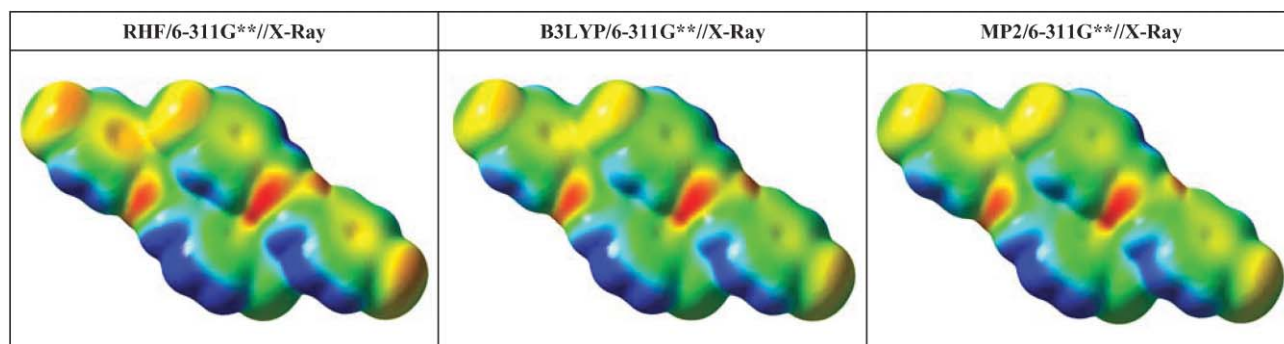


**Fig. 1** Chlorine contacts (in Å). Intralayer Cl...H<sub>a</sub>-C<sub>az</sub>, Cl...H<sub>a</sub>'-C<sub>az</sub>, Cl...H<sub>b</sub>-Ph and Cl...H<sub>b</sub>'-Ph contacts and interlayer Cl...H<sub>c</sub>-Ph and Cl...H<sub>c</sub>'-Ph interactions.

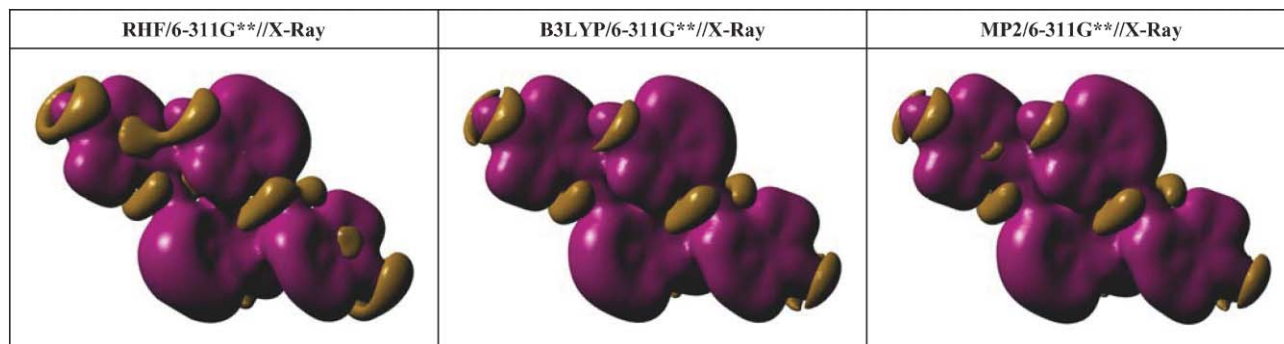
hydrogen bonding. To endorse the more widely inclusive meaning of hydrogen bonding while requesting exclusivity for halogen bonding does create a dilemma.

The measures of success for any bonding model include consistency with the experimental record, generality, and transferability. Therefore, one has to examine whether MPR's suggested definition of halogen bonding satisfies these criteria. MPR would certainly agree that the Ar-I $\cdots$ O=SMe<sub>2</sub> interaction between iodoarenes and dimethylsulfoxide (DMSO) involves halogen bonding. We studied this interaction with

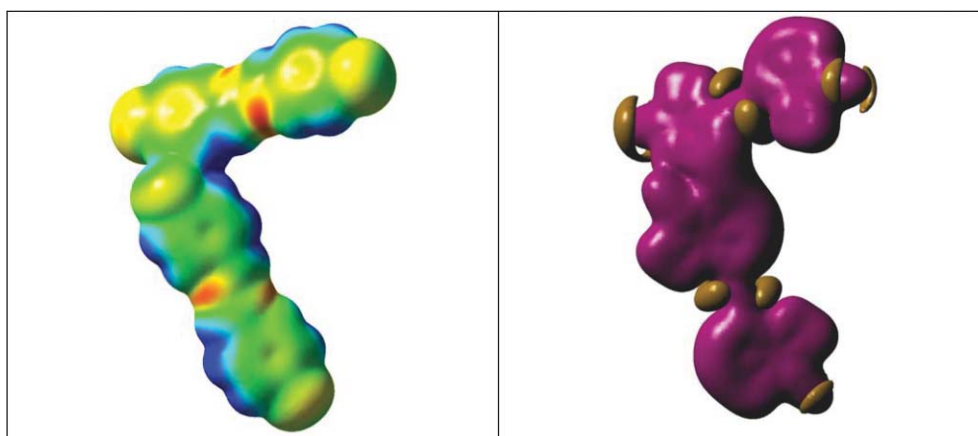
experimental and theoretical methods<sup>16</sup> and found no evidence of Lewis acid–base interaction; oxygen is not a donor, iodine does not act as a acceptor, and there is no intermolecular electron transfer. The leading terms of the interaction are due to charge-induced dipole and dispersion interactions. With regard to generality, one might reasonably doubt whether an extrapolation from studies of Ar-I $\cdots$ O=SMe<sub>2</sub> to Ar-Br $\cdots$ O=SMe<sub>2</sub> would be warranted, and one can be certain that an extrapolation to Ar-X $\cdots$ O=SMe<sub>2</sub> (X = F, Cl) is not warranted.



**Fig. 2** The electrostatic potential mapped on the electron density isosurface of the intralayer azine pair “orange”. The isocontour surface is shown for 0.0004 e a.u.<sup>-3</sup> and the electrostatic potential varies between -0.025 (red) and +0.025 (blue) a.u.



**Fig. 3** Isosurfaces of the electrostatic potential of the intralayer azine pair “orange” computed at three levels of electronic structure theory. The isocontour surfaces are shown for the electrostatic potentials +0.013 (purple) and -0.013 a.u.



**Fig. 4** The electrostatic potential mapped on the electron density isosurface (left) and the isosurface of the electrostatic potential of the interlayer azine pair “blue” computed at MP2/6-311G\*\*//X-Ray. Level settings are as in Fig. 2 and 3.

Progress in solid state chemistry requires progress in the characterization of intermolecular bonding. Tremendous progress has been made in crystallography and information access technology and this progress has allowed for large scale overviews and data mining since the early 1970s.<sup>17</sup> Much less progress has been made with regard to the characterization of the nature of the bonding in the solid state. Combined X-ray and neutron diffraction studies yield direct information about electron density distributions but these methods are not routine. Yet, many other methods including solid state NMR spectroscopy, vibrational spectroscopy, optical spectroscopy, and so on, are easily employed and they all provide ways to learn about electronic structure in the solid state. Electronic structure theory is a powerful tool to supplement, complement, and guide experimental studies of bonding with *ab initio* studies of molecules and clusters<sup>18</sup> and even of periodic systems.<sup>19</sup> Application of electronic structure theory have long been impeded by computational demands. But the hardware barrier is rapidly crumbling and in Table 1 and Fig. 2–4 we show results of calculations of azine pairs obtained with restricted Hartree–Fock theory (RHF), hybrid density functional theory (B3LYP), and second-order Møller–Plesset perturbation theory (MP2). These calculations were performed with the 6-311G\*\* basis set and based on the crystal structure.

The RHF and B3LYP pair binding energies all are very small in magnitude ( $<1$  kcal mol<sup>-1</sup>) and only one pair interaction is attractive (pair “green”). The electronic structure methods RHF and B3LYP account for electrostatic and charge transfer intermolecular interactions and the data show these interactions to be very small. The perturbation method MP2 also accounts for dispersion and only the inclusion of dispersion results in sizable pair binding energies. Fig. 2 and 3 illustrate that the molecular properties are affected by the interactions with neighbors and that these changes significantly affect the chlorine’s anisotropy. Chlorine’s “halo” becomes more anisotropic (pseudo  $\pi$ -symmetry) at the correlated levels, and, more importantly, as soon as a chlorine faces an arene, its halo all but disappears in the direction of the arene (Fig. 3) or it disappears altogether (Fig. 4).

Germany’s greatest poet wrote “Namen sind wie Schall und Rauch” and Goethe’s quote entered the English language in the form of the idioms<sup>20</sup> “What’s in a name?” and “A rose by any other name would smell as sweet”. Samland<sup>21</sup> pointed out

that Goethe used “Name” as synonym for “Wort”. While Goethe stood for meaning over terminology, marketing relies on exclusive terminology. An acceptable balance requires that terminology retains as much meaning as possible and not be exclusive for the sake of branding. Knowledge about the nature of the bonding is additional knowledge and provides detail, and this knowledge should not be used to exclude the naming of the interaction based on structure alone.

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