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Halogen Bonds Stabilised by an Electronic Exchange Channel

Matias O. Miranda^[a, b] and Darío J. R. Duarte^{*[a, b]}*Dedicated to Professor Nérida M. Peruchena*

The σ -hole is an important concept which has been widely used lately to describe the halogen bond (XB) essentially as electrostatic in nature. However, this idea is not free of controversy. For the sake of this work, localised molecular orbital energy decomposition analysis (LMOEDA), interacting quantum atom (IQA) method and analysis of the electrostatic potential have been applied to O–Cl...B (B=CO, PH₃, SH₂, CS, NH₃, OH[−]) complexes. The results show that in their equilibrium geometry the stabilizing effect that arises from the Pauli exclusion principle is larger in magnitude than the electrostatic interactions. Besides, it appears that an electronic exchange channel is established at a certain approach distance between the monomers.

It is well known that halogenated oxides (OI, OBr, OCl and at a lesser extent the OF) play an important role in the chemistry and oxidising capacity of the troposphere.^[1] The interacting halogen bonding that these oxides can form have peculiar characteristics. Zhu et al. have studied the solvation of a BrO radical using adaptive buffered force quantum mechanics/molecular mechanics (QM/MM) dynamics simulations. Their results show that "...the BrO radical prefers to be solvated at the surface of the water slab, rather than the interior region of the water slab despite its high affinity to water".^[2] Besides, two types of OBr-OH₂ contacts were observed (see figure 4a, complex3 and complex9 of reference 2), complex3 seems to be a classic halogen bonds (XBs), while in complex9 the Br atom interacts with two O atoms. Gálvez and Gómez have studied the hydrates of chlorine monoxide [ClO-(H₂O)_n, n=1-6] by means of DFT (B3LYP) and ab initio [MP2 and CCSD(T)] methods with large sets of base functions. They have found two different intermolecular interactions, conventional hydrogen bonds and OCl-OH₂ contacts. Some of these latter interactions have the typical geometric characteristics of XBs,

while others present considerable deviations compared from the conventional XBs of 180 degrees.^[3]

The σ -hole is an important concept which has been widely used lately to describe non-covalent interactions between a covalently-bonded atom of groups IV–VII in the periodic table and a Lewis base.^[4,5] This concept was first used by Politzer et al. for describe to XBs. Then, Clark, Murray and Politzer showed that known features of XBs can be understood through the electrostatics/polarization plus dispersion interpretation.^[5–8]

There is a large number of studies based on the σ -hole concept that allowed the IUPAC to establish that XBs are primarily electrostatic in nature.^[9] However, Stone showed that the geometries of the XBs are not always determined by the electrostatic component.^[10] Syzgantseva et al revealed that the exchange component is very important for the stabilisation of these complexes in their equilibrium geometries.^[11] Bartashevich et al and Bora et al found that bifurcated XBs presents a strong covalent character.^[12,13] Moreover, we have recently shown that some XBs are quantum in nature. In this same work, we have also shown that the σ -hole magnitude can be interpreted as a channel that facilitates the electronic exchange between interacting atoms.^[14]

On the other hand, from the works of Tsirelson et al,¹⁵ Gadre et al¹⁶ and Salahub et al¹⁷ the topology of the electrostatic potential [$\phi(r)$] has shown to be a reliable tool, especially to understand the role of electrostatic in molecular interactions.^[18–21] For example, the stability of anion-anion interactions bound by hydrogen bonds (HBs) in gas phase has been explained by attractive forces localized in a volume situated in the intermolecular region of the HB and defined as the electrostatic attraction region (EAR). This region was determined by the topological analyses of the electron density and of the $\phi(r)$, and by the electric field lines (EFL).^[18] A nucleophilic region of a Lewis base on a surface of the molecule can be revealed as a minimum with negative value, on the topology of $\phi(r)$.^[18] Besides, the $\phi(r)$ has been shown, for non-covalent interactions, to have positive values between two interacting atoms.^[14,22] So, it is interesting to see how the topology of $\phi(r)$ function varies during the formation of XBs as well as their relationship with some energy decomposition analysis (EDA) components. For this purpose, we have studied the selected complexes among the halogenated oxide OCl and the Lewis bases CO, PH₃, SH₂, CS, NH₃ and OH[−].

[a] M. O. Miranda, Dr. D. J. R. Duarte

Laboratorio de Estructura Molecular y Propiedades, Instituto de Química Básica y Aplicada del Nordeste Argentino (UNNE-CONICET)
Avenida Libertad 5460, (3400) Corrientes, Argentina

[b] M. O. Miranda, Dr. D. J. R. Duarte

Departamento de Química, Facultad de Ciencias Exactas y Naturales y Agrimensura, Universidad Nacional del Nordeste, Avenida Libertad 5460, (3400) Corrientes, Argentina
E-mail: djr_duarte@hotmail.com

All geometries were obtained at M062X/aug-cc-pVTZ level of theory using the Gaussian 09^[23] suite of programs. Equilibrium structures were confirmed to be true minima by the absence of any imaginary frequencies. Topological analysis of $\phi(r)$ was performed with Multiwfn program.^[24] LMOEDA^[25] scheme has been carried out with the GAMESS program^[26] at MP2/aug-cc-pVTZ level. IQA analysis was performed at M062X/aug-cc-pVTZ. The accuracy of IQA energies were calculated and the difference between IQA based molecular energies and DFT unpartitioned energies range between 0.2 and 1.6 kJ mol⁻¹. Restricted open-shell methods were applied to the radical species.

In several EDAs scheme is usual practice to join the components that arise from the Pauli exclusion principle (exchange and repulsion) in a single term. However, it is important that both contributions maintain their individuality. In the LMOEDA method, pure exchange energy is obtained from orthogonal functions, while non-orthogonal and orthogonal functions are used to define the repulsion energy.^[27]

The LMOEDA partition method has been carried according to the equation below:

$$E_i(\text{LMOEDA}) = E_{\text{el}} + E_{\text{ex}} + E_{\text{rep}} + E_{\text{pol}} + E_{\text{disp}}$$

where $E_i(\text{LMOEDA})$ is the interaction energy, E_{el} is the electrostatic component, E_{ex} is the attractive exchange component and E_{rep} is the repulsive term, both resulting from the Pauli

exclusion principle, E_{pol} and E_{disp} correspond to polarization and dispersion terms, respectively. In this work only E_{el} and E_{ex} terms have been used. Figure 1 exhibits the energetic variations of these components and the values of $\phi(r)$ determined over a critical point (CP) of the topology of $\phi(r)$ (V_{CP}), both as a function of the intermolecular distance.

It is clearly seen that at great distances the $E_{\text{el}} > E_{\text{ex}}$ and at lower distances this trend is reversed. At equilibrium distance, E_{ex} over E_{el} predominates. This last observation has already been observed in other strong^[28] and weak/moderate^[14] interactions.

As we have already mentioned above, the topological analysis of the $\phi(r)$ function is a useful tool to study the role of electrostatic forces in molecular interactions. This analysis is based on the identification and location of the CPs. That is, the points at which the gradient of $\phi(r)$ is canceled [$\nabla\phi(r)=0$]. As in the $\rho(r)$ topology nondegenerate CPs can be (3,-3), (3,-1), (3,+1), (3,+3). The first of them corresponds to the nuclear positions, the second and the third correspond to saddle points and the last corresponds to local minima. These last are commonly associated with lone pairs (LPs). We have studied the variation of $\phi(r)$ over the LP (V_{CP}) of the Lewis base when the complexes are being formed (see Figure 1). The green curve shows the variation of V_{CP} over (3,+3)/(3,+1)/(3,-1) CP. These points are indicated with blue dots, yellow dots and green dots respectively. It is observed that, as the monomers approach the intersection of the E_{el} and E_{ex} curves, V_{CP} begin to

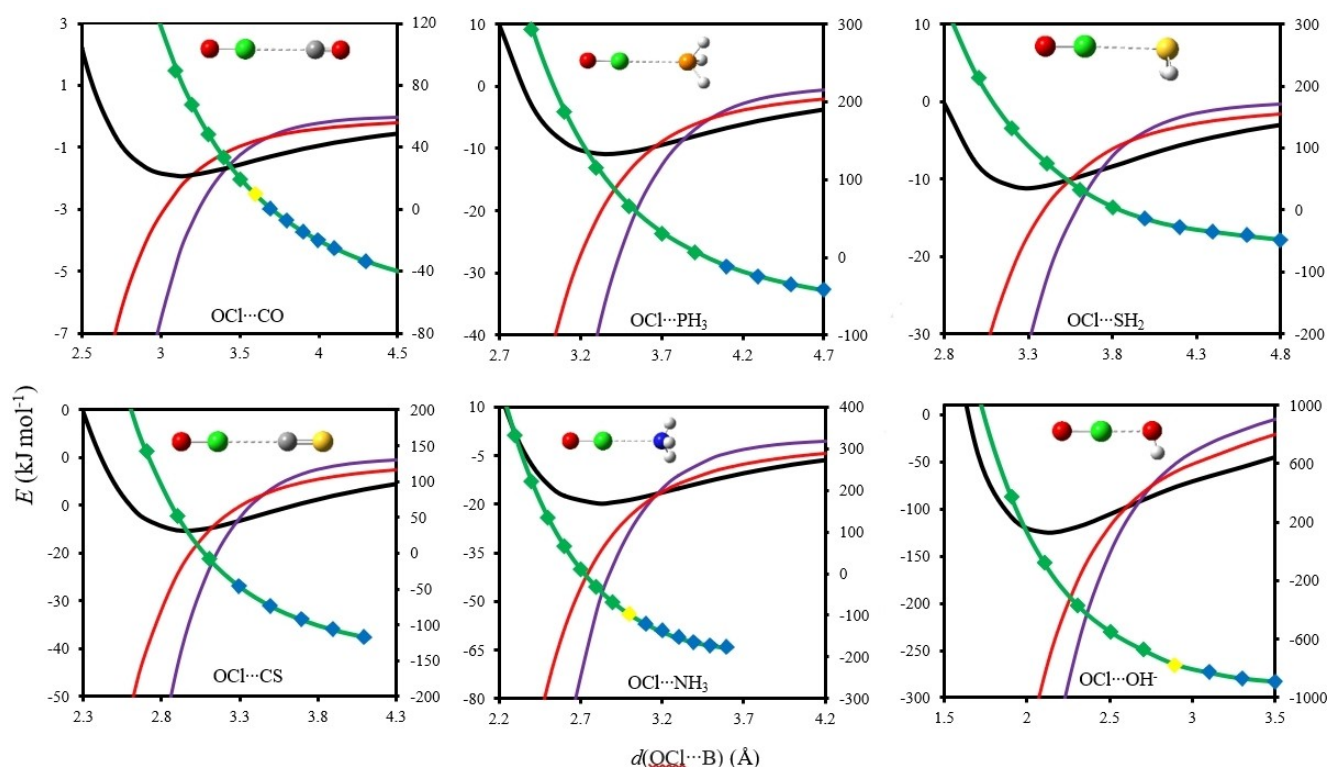


Figure 1. Variation of E_i , LMOEDA (black line), E_{el} (red line) and E_{ex} (purple line) on the left energy scale and V_{CP} (green/blue line) on the right energy scale over C/P/S/ N/O atom in OX...B system. Blue dots indicate (3,+3) CPs, yellow dot indicates (3,+1) CP and green dots are (3,-1) CPs of the topology of $\phi(r)$. The critical point is on direction of interaction.

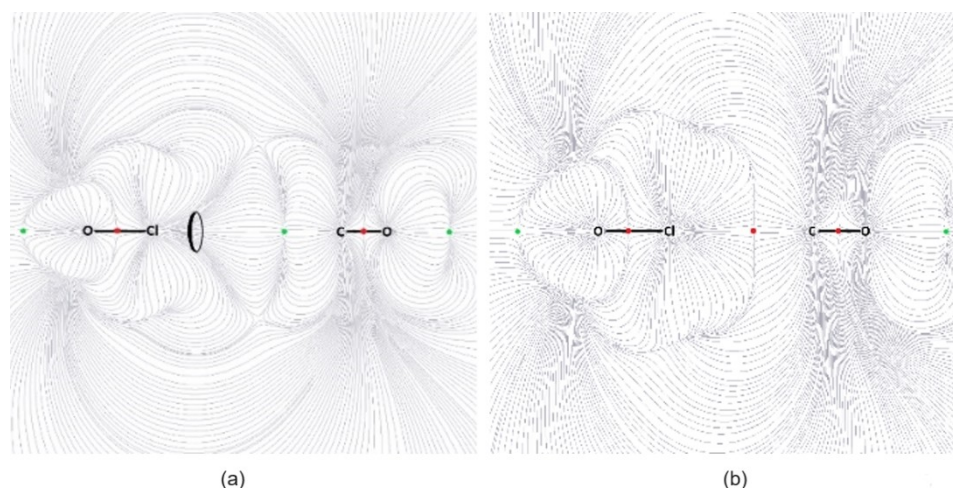


Figure 2. EFLs of the OCl-CO dimer at 5.0 Å (a) and its equilibrium geometry at 3.1 Å (b) are showed. The green and red dots indicate (3,+3) and (3,-1) CPs respectively of the topology of $\phi(r)$.

decrease in magnitude, passing later from negative to positive values. In this region (3,+3) CP goes to (3,+1) CP, in some cases, and then to (3,-1) CP. That is, the local minimum of the Lewis base (LP) disappears, giving rise to a (3,-1) CP of $\phi(r)$ (red dot in figure 2b). Therefore, it appears that the topology of $\phi(r)$ provides the time in which the electrostatic forces leave being the predominant ones and begin to predominate the forces of quantum origin. This allows us to establish that in these selected XBs, approximately at the distance where curves E_{el} and E_{ex} intersect, a channel that facilitates electronic exchange between the monomers is established. Pendás et al. showed something similar through the Quantum Theory of Atoms in Molecules (QTAIM).^[29] These researchers showed that the bond path (BP) is a privileged exchange channel between two interacting atoms.^[30] Logically, in the complexes studied here a BP and a bond critical point (BCP – obtained from QTAIM) among the C/P/S/N/O and Cl atoms is established, which indicates that there is a binding interaction between them. Topological parameters in these CPs are typical of closed-shell interactions. According to Bader and Essén “these interactions are dominated by the contraction of charge away from the interatomic surface towards each of the nuclei”.^[31]

The electric field lines (EFLs) indicate the direction in which the Coulombic forces act on $\rho(r)$. Figure 2 shows these lines for the OCl-CO dimer at 5.0 and 3.1 Å (equilibrium geometry). At distances away from the equilibrium position (see figure 2a), it is observed that there are EFLs that begin at the minimum of topology of $\phi(r)$ [(3,+3) CP-green dot] close to the C atom and end at the nucleus of Cl or C (source and sinks). Looking at these EFLs at the region near the Cl atom reveals that all of them pass through a narrow region localised at the outer region of the halogen atom in the direction of the O-Cl bond (black oval). This observation is clearly in accordance with the σ -hole concept.

The lone pairs (LPs) can be detected by the topology of $L(r) = -\nabla^2\rho(r)$. However, a fundamental difference is observed

when we use the topology of $\phi(r)$. In the topology of $L(r)$ the maximum associated with LP remains when the complex has been formed,^[32,33] while in the topology of $\phi(r)$ it disappears (see figure 2). This last observation could be giving us information about the moment, during dimer formation, in which the electrostatic forces leave being the predominant ones.

To compare the results of the LMOEDA scheme, we carried out an IQA analysis^[34] on the equilibrium geometry. This scheme takes into account the Fermi hole, which is a consequence of the Pauli principle.^[27] The IQA method is a powerful tool to characterize the nature of intermolecular interactions. The interaction energy, $E_i(\text{IQA})$, can be decomposed in three contributions: deformation (E_{def}), Coulomb (V_{cl}) and correlation-exchange (V_{xc}) terms:

$$E_i(\text{IQA}) = E_{def} + V_{cl} + V_{xc}$$

Table 1 shows the results obtained. In all these cases, it is clearly seen that quantum effects (V_{xc} component) are the most important ones. This last affirmation contrasts with a large

Table 1. Intermolecular IQA contributions and total interaction energy at equilibrium geometries.

Dimers	$E_{def}^{[a]}$ [kJ mol ⁻¹]	$V_{cl}^{[b]}$ [kJ mol ⁻¹]	$V_{xc}^{[c]}$ [kJ mol ⁻¹]	$E_i(\text{IQA})^{[d]}$ [kJ mol ⁻¹]
OCl-CO	42.3	-3.3	-44.8	-5.7
OCl-PH ₃	54.1	-3.8	-59.5	-9.1
OCl-SH ₂	54.1	-4.5	-59.6	-10.1
OCl-CS	59.4	-8.8	-61.2	-10.6
OCl-NH ₃	75.7	-18.5	-77.1	-19.9
OCl-OH ⁻	262.7	-54.0	-348.6	-139.9

[a] E_{def} : deformation energy. [b] V_{cl} : coulombic interaction energy. [c] V_{xc} : exchange-correlation energy. [d] $E_i(\text{IQA})$: total interaction energy between monomers.

number of works that show that XBs are electrostatic in nature.^[35] However, it is in agreement with observations performed by Bartashevich et al and Bora et al who studied some XBs using IQA analysis.^[12,13] These researchers have found that bifurcated halogen bonding have a high covalent character ($V_{xc} \gg V_{cl}$). Syzgantseva et al also studied some XBs using this methodology.^[11] They found that the E_{xc}/E_{el} ratio are equal to 0.8 and 1.2 for the FBr-NH₃ and FBr-OH⁻ complexes, respectively. While, in the present work these ratios range between 4.2 and 15.6. Therefore, the XBs studied here have a strong covalent character.

It is important to note that a very good linear relationship has been found between $E_1(\text{IQA})$ and $E_1(\text{LMOEDA})$ ($R=1.00$) at equilibrium geometry.

The delocalization index $\text{DI}(\text{Cl}, \text{Y})$ (with $\text{Y} = \text{C/P/S/N/O}$) is a measure of the number of electrons exchanged or shared between interacting atoms and V_{xc} can be interpreted as a measurement of the exchange contribution (derived of the Pauli exclusion principle) between interacting molecules. As expected, due to the relationship that exists between these two magnitudes,^[36] a very good linear correlation was found (figure not shown, $R^2=1.00$).

The $\phi(r)$ is a measure of the electrostatic forces between a positive test charge and the undisturbed molecule or molecular sistema, without considering the induction and dispersion effects.^[37] As is well-known, the $\phi(r)$ mapped over an isosurface of the electron density provides valuable information about the susceptible sites to nucleophilic [$\phi(r)_{\text{max}}$] and electrophilic [$\phi(r)_{\text{min}}$] attack. Moreover, there are a large number of studies where the σ -hole concept explains very well the strength of XBs and other interactions.^[35] Figure 3 shows the $\phi(r)$ maps for the OCl-CO complex at 5.0 and 3.1 Å (equilibrium geometry). These maps have been performed on the isosurfaces of the electron density corresponding to an isocontour slightly exceeding the value of the electron density at the Cl-C BCP of atom in molecule theory. At far distances it is observed clearly the interaction between $\phi(r)_{\text{max}}$ of the Cl atom and $\phi(r)_{\text{min}}$ of the C atom (see Figure 3a). That is, a maximum on the isosurface of the Cl atom and a minimum on the isosurface of the C atom. While, at the equilibrium geometry this complementary is not observed. The most dramatic change is observed over the LP of the C atom, this goes from being a minimum at 5 Å [$\phi(r) = -40.0 \text{ kJ mol}^{-1}$] to a maximum at the

equilibrium geometry [$\phi(r) = 106.8 \text{ kJ mol}^{-1}$]. In the epicenter of σ -hole and of the LP only positive values are observed (two maxima). It draws a lot of attention that in the region of the LP of the CO a pseudo σ -hole has been created (see figure 3b). This is probably due to the inter-electronic repulsion between the LP of the CO and the charge density accumulation around the halogen atom. Moreover, in process of complex formation the $\phi(r)$ on σ -hole of OCl has decreased, probably due to charge transfer from LP of CO to $\sigma^*_{(\text{O-Cl})}$, characteristic of the XBs. Similar observation has been carried by Bartashevich and Tsirelson^[22] in classical XBs, who state that "...the anisotropy of the $\phi(r)$ between the neighboring molecules carries the information about the whole system. In this case, the characteristics of $\phi(r)$ in the region of non-covalent interactions, as a rule, acquire the blurred meaning". We interpret that the appearance of this pseudo σ -hole on surface of the CO molecule could be an indication of formation of an electronic exchange channel. In addition, in the same work these authors have also studied the exchange electronic through of the potential acting on an electron in a molecule (PAEM). They claim that "the lower PAEM barrier, the easier neighboring atoms share electrons and the more significant covalence of the bond between them." In other words, the greater the electronic exchange between interacting atoms, the stronger the bonds will be. This observation is accordance with results found by IQA analysis (see table 1)

Figure 3 also shows the electronic changes on the LPs of the oxygen atoms. At the equilibrium geometry, the $\phi(r)$ has increased in absolute value with respect to the distant dimer. Another important thing to observe is, that the OCl specie does not present a symmetric charge concentration around the Cl atom, as in the monovalent halides. Escribano et al. have shown through experimental and theoretical studies, that the O-Cl bond have a certain double bond character.^[38] So, it is expected that some sp^2 hybridization character for Cl atom, with two defined LPs.

The results presented in this short communication are in agreement with the ideas recently presented by Pendás et al. for covalent bonds. They state that "Bonds and chemical dashes are short-range constructions, intimately connected with exchange-correlation (or covalent) interaction energies, and thus, with electron delocalization. However, whenever charge flow

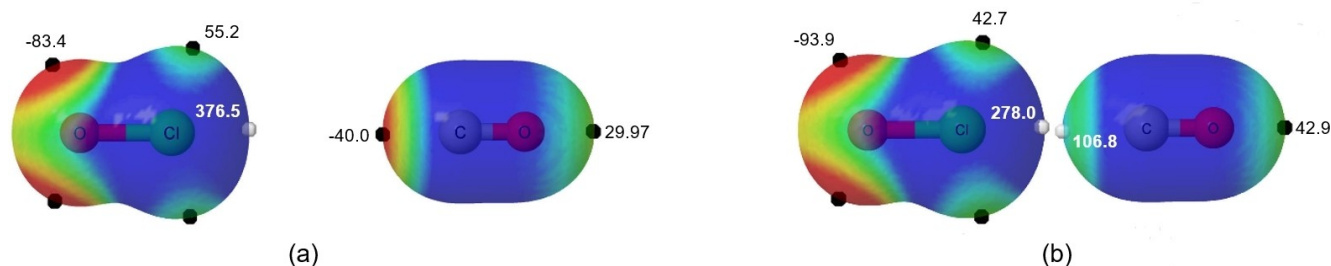


Figure 3. Electrostatic potential maps on the 0.012 au electron density isosurface of OCl-CO complex at 5.0 (a) and 3.1 Å (b). The range of colors vary between red and blue corresponds to the values of the $\phi(r)$ between -26.3 and 131.3 kJ/mol , respectively. The black and white dots represent the location of the $\phi(r)_{\text{min}}$ and $\phi(r)_{\text{max}}$ respectively.

(charge transfer, electron density polarization, etc.) occurs within a system, Coulombic terms necessarily appear^[39].

In conclusion, we have reported the relationship between some parameters of $\phi(r)$ and the quantum and classical effects obtained with LMOEDA and IQA schemes. At the geometry of equilibrium, the stabilizing effect that arises from the Pauli exclusion principle is larger in magnitude than the electrostatic interactions. Coulombic forces are important at long range and they are in accordance with σ -hole concept. The variations of V_{CP} over the LP of the Lewis base in conjunction with the variations of E_{el} and E_{ex} terms of LMOEDA scheme with the intermolecular distance seem to indicate that an electronic exchange channel is established at a certain approach distance between the monomers. Finally, the topology of $\phi(r)$ is a reliable tool to detect well-defined lone pairs and to understand in depth the electronic changes that occur in the process of formation of XBs.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] W. R. Simpson, S. S. Brown, A. Saiz-Lopez, J. A. Thornton, R. Von Glasow, *Chem. Rev.* **2015**, *115*, 4035–4062.
- [2] C. Zhu, Y. Gao, J. Zhong, Y. Huang, J. S. Francisco, X. C. Zeng, *J. Chem. Phys.* **2016**, *145*, 1–4.
- [3] O. Gálvez, P. C. Gómez, *Chem. Phys. Lett.*, **2007**, *448*, 16–23.
- [4] S. J. Grabowski, W. A. Sokalski, *ChemPhysChem* **2017**, *18*, 1569–1577.
- [5] P. Politzer, J. S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178–11189.
- [6] P. Politzer, K. E. Riley, F. A. Bulat, J. S. Murray, *Comput. Theor. Chem.* **2012**, *998*, 2–8.
- [7] T. Clark, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2013**, *3*, 13–20.
- [8] P. Politzer, J. S. Murray, *ChemPhysChem* **2013**, *14*, 278–294.
- [9] G. R. Desiraju, P. Shing Ho, L. Kloos, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure Appl. Chem.* **2013**, *85*, 1711–1713.
- [10] A. J. Stone, *J. Am. Chem. Soc.* **2013**, *135*, 7005–7009.
- [11] O. Syzgantseva, V. Tognetti, L. Joubert, *J. Phys. Chem. A* **2013**, *117*, 8969–8980.
- [12] E. Bartashevich, E. Troitskaya, Á. M. Pendás, V. Tsirelson, *Comput. Theor. Chem.* **2015**, *1053*, 229–237.
- [13] P. L. Bora, M. Novák, J. Novotný, C. Foroutan-Nejad, R. Marek, *Chem. Eur. J.* **2017**, *23*, 7315–7323.
- [14] D. J. R. Duarte, G. J. Buralli, N. M. Peruchena, *Chem. Phys. Lett.* **2018**, *710*, 113–117.
- [15] A. A. Baskakov, A. A. Varnek, V. G. Tsirelson, R. P. Ozerov, *J. of Struct. Chem.* **1985**, *25*, 636–37.
- [16] S. R. Gadre, S. A. Kulkarni, I. H. Shrivastava *J. Chem. Phys.* **1992**, *96*, 5253–5260.
- [17] B. Christophe, M. Defranceschi, J. Delhalle, G. Lécayon, D. R. Salahub, *THEOCHEM* **1995**, *330*, 279–285.
- [18] I. Mata, E. Molins, I. Alkorta, E. Espinosa, *J. Phys. Chem. A* **2015**, *119*, 183–194.
- [19] I. Mata, E. Molins, I. Alkorta, E. Espinosa, *J. Phys. Chem. A* **2007**, *111*, 6425–6433.
- [20] I. Mata, I. Alkorta, E. Molins, E. Espinosa, *ChemPhysChem* **2012**, *13*, 1421–1424.
- [21] I. Mata, I. Alkorta, E. Molins, E. Espinosa, *Chem. Phys. Lett.* **2013**, *555*, 106–109.
- [22] E. Bartashevich, V. Tsirelson, *J. Comput. Chem.* **2017**, *39*, 573–580.
- [23] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT 2013.
- [24] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.
- [25] P. Su, H. Li, *J. Chem. Phys.* **2009**, *131*, 1–15.
- [26] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, *J. Comput. Chem.* **1993**, *14*, 1347–1363.
- [27] J. L. Sainz, A. Martín Pendás, E. Francisco, *Quantitative Determination of the Nature of Intermolecular Bonds by EDA Analysis in Intermolecular Interactions in Crystals: Fundamentals of Crystal Engineering* (Ed: Juan J. Novoa), The Royal Society of Chemistry, London, **2018**, p. 178.
- [28] D. J. R. Duarte, M. S. Miranda, J. C. G. E. Da Silva, J. F. Liebman, *Struct. Chem.* **2016**, *27*, 1743–1751.
- [29] R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon, Oxford, U K, **1990**.
- [30] A. Martín Pendás, E. Francisco, M. A. Blanco, C. Gatti, *Chem. Eur. J.* **2007**, *13*, 9362–9371.
- [31] R. F. W. Bader, H. Essen, *J. Chem. Phys.* **1984**, *80*, 1943–1960.
- [32] G. J. Buralli, D. J. R. Duarte, G. L. Sosa, N. M. Peruchena, *Struct. Chem.* **2017**, *28*, 1823–1830.
- [33] G. J. Buralli, D. J. R. Duarte, N. M. Peruchena, *Chem. Nova* **2016**, *39*, 676–685.
- [34] M. A. Blanco, A. M. Pendás, E. Francisco, *J. Chem. Theory Comput.* **2005**, *1*, 1096–1109.
- [35] G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, *116*, 2478–2601.
- [36] P. Maxwell, Á. M. Pendás, P. L. A. Popelier, *Phys. Chem. Chem. Phys.* **2016**, *18*, 20986–21000.
- [37] G. Náray-Szabó, G. G. Ferenczy, *Chem. Rev.* **1995**, *95*, 829–847.
- [38] R. Escibano, R. Mosteo, P. Gómez, *Can. J. Phys.* **2001**, *79*, 597–609.
- [39] A. M. Pendás, J. L. Casals-Sainz, E. Francisco, *Chem. Eur. J.* **2019**, *25*, 309–314.

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