On the Uselessness of Bond Paths Linking Distant Atoms and on the Violation of the Concept of Privileged Exchange Channels

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We refer to frequently used determinants suggesting dominant interactions between distant atoms in various dimers. First of all, we show, against the still-prevailing opinion, that, in general, bond paths have nothing in common with dominant intermolecular interactions and therefore they are useless in such cases. Quite the contrary, reliable information about dominant intermolecular interactions can be obtained by means of electrostatic potential maps, which very convincingly explain mutual orientation of molecules in a dimer. For the first time, numerous examples of interactions that violate both the concept of privileged exchange channels proposed by Pendás and his collaborators as well as inequalities obtained by Tognetti and Joubert for the β parameter related to secondary interactions are presented. The possible cause of this violation is suggested. We also show that the so-called counterintuitive bond paths result from quite natural behavior of the electron density gradient vector, i.e. searching for those areas of space that are characterized by large values of electron density or the most expanded its distributions.

1. Introduction

Quantum Theory of Atoms in Molecules (QTAIM) introduced by Bader[1–7] has gained significant importance in the theory of chemical bond and intermolecular interactions due to its beauty, the unique opportunity of insight into individual atoms, but above all because the simultaneous presence of a bond path (BP) and a bond critical point (BCP) corresponding to any pair of atoms was undoubtedly to indicate the presence of a bond between this pair of atoms. Indeed, in the vast majority of simple and isolated molecules, molecular graphs (i.e., networks of bond paths) turn out to be consistent with structural formulas drawn by chemists[2] based on expected, mainly on the basis of atomic valencies, locations of chemical bonds. Unfortunately, this caused a lot of trust in QTAIM and the automatic and uncritical treatment of a bond path as an indicator and even proof of the existance of chemical bond, although the chemical bond itself is not a strictly defined concept.[8–10] Much later,[7] Bader alleviated this equality[3] by proclaiming that the presence of a bond path should *not* be understood as the presence of a chemical bond (particularly in the Lewis sense) since "is neither measurable nor susceptible to theoretical definition and means different things to different people", but rather as a topological proof that atoms are bonded to one another since bond path is a measurable property of a system.[1,6,7] To distinguish these two rather subtle issues, Bader proposed using the terms *bond* and *bonding* to the former and latter case, respectively.[7] Although Bader's

intention was to clearly distinguish between "more to feeling than to define" the concept of a chemical bond and precisely defined, thanks to the bond path, binding, in addition to enriching chemistry, this dualism of concepts also seems to unnecessarily introduce confusion around the nature of a chemical bond, and even move away from it. Quite recently, Shahbazian took it rather bluntly: "Bader's proposal is clearly beyond semantics, and if taken seriously, the paper is the manifesto of a comprehensive research programme of rewriting chemistry without using the concept of bond, but the jargon of the QTAIM".[11] Moreover, not seeing the profit from such dualism of concepts, Shahbazian proposed a complete break with referring to the term of bond by modifying the terms "bond path" (BP) and "bond critical point" (BCP) to "line path" and "line critical point", respectively.[11,12] Although we agree with Shahbazian that the BP and BCP terminology is unfavorable, given the fact that each theory has its own terminology and that the terminology used in QTAIM is widely known, we will also use it in this article so as not to cause unnecessary ambiguities and not to duplicate the terms.

Starting from the Cioslowski's articles in the early 1990s,[13–15] numerous publications[16–25] have began appearing in which Bader's concept that the presence of a bond path proves stabilizing effect was criticized. Cioslowski and Mixon announced that sterically crowded systems can also generate bond paths which should be interpreted as being result of repulsive rather than attractive interaction.[13–15] Later on, the same conclusions were made by studies of endohedral complexes He@cubane, He@adamantane and He2@dodecahedrane.[16–19] Nonbonding nature of interactions between pairs of atoms linked by bond paths was, however, also shown in many cases of non-endohedral systems. For example, Haaland et al.[17] found atomic interaction lines (AIL), i.e. counterparts of bond paths in non-equilibrium geometry,

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for a wide range of He···C distances in the He···CH$_4$ dimer. Interaction energies were, however, positive, meaning that the He···C interaction is destabilizing. Similar calculations have also been made recently for water dimers with a helium or neon atom.[25]

The interaction between *ortho*-hydrogens in planar biphenyl[20,21,26] has already become an almost academic example. Destabilizing nature of X···O (X=F, Cl, Br, I), O···O or F···F contacts traced by bond paths have also been shown[22,23] by means of various estimates of interaction energies and appropriate geometric changes taking place during the X···O contact formation or upon flattening of somewhat twisted structures.[22] Then, the destabilizing nature of the X···O contact in ZZ conformer of 3-halogenopropenal has been supported by means of dimer model in which the C—X···O=C fragment was preserved with its orginal geometric arrangement and, most importantly, the interaction energy was well-defined.[23]

As one can see, almost from the very beginning of QTAIM, the interpretation of the presence of a bond path as a proof of stabilizing interaction was quite doubtful. This is especially true for the presence of bond paths in endohedral complexes and between closely spaced atoms, especially strongly electronegative, with same signs of formal atomic charges, where strong interatomic repulsion would rather be expected.[27] The latter case is closely related with the second reason of the interpretative criticism of bond paths and which will be called in this article as counterintuitive[1] bond paths.[28,29] Briefly explaining, this phrase will refer to those bond paths whose presence is unexpected on the basis of other than topological characteristics (geometric, spectroscopic, atomic charges, electrostatic potentials, etc.) of dominant interactions. Such situations will be the main topic of this article and we mention some important literature examples now.

Counterintuitive bond paths of the H···H type were found inside the inner molecular cavity of kekulene[30] and in many other hydrocarbons[14,31,32] as, e.g. planar benzenoids possessing phenanthrene moiety,[14] styrene, Z-2-butene or 2,3-dimethyl-2-butene.[32] As already mentioned, the planar form of biphenyl also features two counterintuitive H···H atomic interaction lines between pairs of *ortho*-hydrogens.[13,14,20,21,26] Counterintuitive C···He bond paths were found in the aforementioned endohedral complexes as, e.g. He@cubane,[16] He@adamantane[17,18] or He$_2$@dodecahedrane.[19] Bond paths between two halogen atoms were found in solid molecular chlorine,[33] perhalogenated cyclohexanes, dodecahedranes and fulleranes,[15] protonated perfluorodiethyl ether,[34] and various difluorinated aromatic compounds as e.g. 1,8-difluoronaphtalene,[35] while bond paths of the halogen-oxygen type were found, e.g., in 3-chloropropenal and its fluoro derivatives.[36] Very important cases of counterintuitive bond paths were found between two closely spaced oxygen atoms, as is the case, for example in C(NO$_2$)$_3^-$ ion,[30,37] open conformers of enol forms of cis-β-diketones[38] and in dimer of carbon dioxide,[33,39] which will be analyzed also in this article. Without doubt, the full list would be very long.

At this point, we must also mention a series of most recent Shahbazian's articles,[11,12,32,40] in which yet further arguments are given for why bond paths cannot be interpreted as indicators of chemical bonds. Namely, molecular vibrations or other even small continuous changes in molecular geometry can change the pattern of bond paths, i.e. molecular graph, since some bond paths may emerge while other may disappear.[12] Moreover, it is known that molecular graph can also change under the change of the level of theory (i.e. the computational method or/and the basis set) used to determine the electron density distribution. According to the orthodox QTAIM,[1] this would mean sudden formation or breaking of bonds. As no one expects sudden formations or breakings of bonds during molecular vibrations or, what is more, changes in the theoretical method only, bond path cannot mean chemical bond.[11,12,29] Moreover, topology of the electron density distribution is mainly governed by atomic densities, whereas the electron density build-up, which is characteristic for covalent bonds, is rather modest.[32,40] Wick and Clark have also shown that the presence of BPs and BCPs results simply from the Poincaré-Hopf relationship and the symmetry of the system and does not necessarily mean binding effect.[25]

It is clear, therefore, that we come to an apparent contradiction regarding the interpretation of a bond path as an indicator of chemical bonding or dominant intermolecular interaction.[29] On the one hand, indeed, in many cases presence of a bond path coincides with the line drawn by chemists in the structural formula of a molecule, on the other hand, however, we have many reports about counterintuitive bond paths. What is more, one can also find many examples showing that bond paths are not created where one would expect this, as different parameters suggest that the given interatomic interaction should be dominant.[29] As an explanation of this seeming puzzle, it will be shown, what the main purpose of this article is, that in general the bond path between distant atoms has nothing to do with the dominant interatomic interactions. These, instead, are suggested by other than topological parameters, mainly being of electrostatic nature.[29]

In the light of this article, it is necessarily to mention that some[41–48] have been trying to explain the presence of bond path by referring to the concept of exchange energy. Namely, using several molecular systems and then introducing a very interesting concept of the so-called privileged exchange channels, Pendás et al.[41] have shown that bond paths form between those pairs of atoms which give greatest energetical gain due to electron spin pairing, even if in some instances this may lead to an overall energy increase. Therefore, according to this concept, the exchange energy would be the most important component of interaction energy, because it would be directly related to the presence of bond path on a molecular graph.[42–47] It is worth mentioning here that, as has been shown,[42,49,50] the exchange energy can be directly used to determine the bond strength.

Despite the attractiveness of the concept of privileged exchange channels[41] and its certain acceptance,[42–48] we will show, however, that this concept is incomplete or even incorrect. The possible cause of the lack of confirmation and

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[1] In our recent articles,[28,29] we used the less successful phrase "unexpected".

possible erroneousness of this concept will also be given. Moreover, we will show that dominant intermolecular interactions should be suggested by values of geometric, spectroscopic and electrostatic parameters and not by the presence of a bond path. In the latter case, attributing too much importance to bond path may lead to completely wrong interpretation.

2. Methodology

The presented conclusions are based on calculations made for 10 unique dimers of E_1CE_2 (where E_1 and E_2 is oxygen and/or sulphur) (**A1**–**A10**), 12 parallel dimers of the $(HBeX_1)\cdots(X_2BCl_2)$ form (where $X_1 \in \{H, F, Cl, Br\}$ and $X_2 \in \{F, Cl, Br\}$) (**B1**--**B12**) and 6 parallel dimers of the $(HMgX_1)\cdots(X_2BCl_2)$ form (where $X_1 \in \{Cl, Br\}$ and $X_2 \in \{F, Cl, Br\}$) (**C1**–**C6**). This wide collection of dimers (see Figure 1) presents different patterns of bond paths tracing
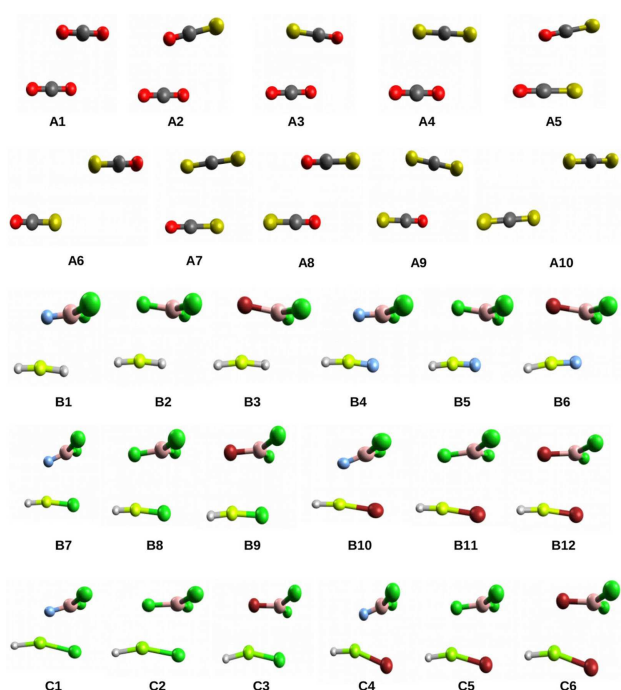

Figure 1. Fully optimized geometries (M06-2X/aug-pc-2) of investigated dimers. Colours of atoms are as follows: C – black, O – red, S – yellow, H – white, B – pink, F – blue, Cl – green, Br – dark red, Be – pea-green, Mg – greenish.

intermolecular interactions between both interacting monomers. Geometry optimizations and energy decompositions based on the method of Interacting Quantum Atoms (IQA)[51–53] were performed by means of the M06-2X[54] exchange-correlation functional of Density Functional Theory (DFT)[55,56] in conjunction with the aug-pc-2 basis set.[57–60] M06-2X is one of two (next to B3LYP) non-local exchange-correlation functionals supported by AIMAll[61] for full and accurate IQA-based calculations and the polarization-consistent basis sets introduced by Jensen (pc-*n*) were optimized for calculations based on DFT.[62]

AIMAll was also used for topological analysis of electron density distribution based on QTAIM.

No imaginary frequencies were obtained meaning that all the considered dimer geometries correspond to minima on potential energy hypersurfaces. Geometry optimizations were performed using Gaussian 09 program,[63] during which the cutoffs on forces and step size, which are used to determine convergence, were additionally tightened to 0.000015 and 0.000010 for maximum force and its root mean square, respectively, and 0.000060 and 0.000040 for maximum displacement and its root mean square, respectively. Moreover, the integration grid was additionally increased to the (99,590) one (UltraFine) having 99 radial shells and 590 angular points per shell.

IQA is deeply rooted in QTAIM[1] and was introduced by Pendás, Blanco and Francisco[51–53] to partition the total energy of a molecular system into some intra- and interatomic terms by direct computing of one- and two-electron components. Among the many energy terms available within IQA, the most important one will be the interatomic interaction energy given by eq. 1

$$E_{int}^{E_1E_2} = V_{nn}^{E_1E_2} + V_{en}^{E_1E_2} + V_{ne}^{E_1E_2} + V_{ee}^{E_1E_2} \quad (E_1 \neq E_2) \tag{1}$$

where $V_{nn}^{E_1E_2}$ is the repulsion energy between nuclei of atoms E_1 and E_2, $V_{en}^{E_1E_2}$ is the attraction energy between electrons of the atom E_1 and the nucleus of the atom E_2, $V_{ne}^{E_1E_2}$ is the attraction energy between the nucleus of the atom E_1 and the electrons of the atom E_2, and $V_{ee}^{E_1E_2}$ is the repulsion energy between the electrons of the atom E_1 and the electrons of the atom E_2 (i.e., the interatomic two-electron interaction energy), which can be further decomposed into its Coulomb and exchange-correlation terms[51] according to eq. 2

$$V_{ee}^{E_1E_2} = V_{ee,C}^{E_1E_2} + V_{ee,xc}^{E_1E_2} \tag{2}$$

Adding $V_{ee,C}^{E_1E_2}$ to the first three terms of eq. 1 gives the so-called classic (electrostatic) interaction energy

$$V_{elst}^{E_1E_2} = V_{nn}^{E_1E_2} + V_{en}^{E_1E_2} + V_{ne}^{E_1E_2} + V_{ee,C}^{E_1E_2} \tag{3}$$

Hence, the interatomic interaction energy can finally be written as

$$E_{int}^{E_1E_2} = V_{elst}^{E_1E_2} + V_{ee,xc}^{E_1E_2} \tag{4}$$

As can be seen, all the energy terms of eqs. 1–2 have well-defined physical meanings and, importantly, the interatomic interaction energy, $E_{int}^{E_1E_2}$, can be computed for any pair of atoms E_1 and E_2.

It should be emphasized that, in contrast to the previously[22,23,64–67] used methods of calculating interaction energies, $E_{int}^{E_1E_2}$ does not require any reference systems, therefore IQA is a non-invasive method. It was successfully used to describe various interatomic contacts as diverse types of bonds in simple molecules,[42,51,52] inter-[42,53] and intramolecular[43,44] hydrogen bonds and H⋯H,[41] He⋯C,[47] anion-anion, and cation-

cation interactions.[46] In our studies we focus on those pairs of atoms that either are linked by a counterintuitive bond path or are supposed to strongly interact with each other but are not linked with each other by a bond path.

3. Results and Discussion

It has been shown that the exchange energy can be directly used to determine the bond strength.[42] Because according to Bader (at least according to his early articles) the presence of bond path was to mean the presence of bond(ing) and some stabilization of it, it probably contributed to attempts to link bond path with the exchange energy.[41–48] However, it is not clear to us why such a relationship would be to exist at all. We will come back to this issue later.

While temporarily accepting the general truth of the relationship (however doubtful) between bond path and exchange energy,[41] it is obvious that due to the short-range nature of the exchange energy its role becomes negligible for further interatomic distances. Also for this reason, the treatment of bond path as indicator of dominant intermolecular interaction is erroneous. Furthermore, due to the much slower decay of the electrostatic energy, this component becomes much more important and gains the advantage of predicting dominant intermolecular interactions.[29] For this reason, the use of various electrostatic parameters (as atomic charges or molecular electrostatic potentials) to find dominant intermolecular interactions is fully justified.[28,29,68–78]

3.1. Uselessness of Bond Paths

We will now show that the bond paths linking distant atoms, e.g. belonging to two interacting molecules, are useless, because they carry virtually no valuable information about the dominant interaction. Let us have a look at molecular graphs of the considered dimers shown in Figure 2 (where the numbering of atoms used is also shown). In **A1**–**A10**, in all cases except **A4**, **A7** and **A9** there are bond paths linking E3 and E4 atoms. Although the molecular graphs obtained for **B1**–**B12** and **C1**–**C6** are generally somewhat more complex, on many of them one can notice bond paths specific for interactions H···X or/and X···X (where X is a halogen atom). It must be emphasized that these bond paths are counterintuitive, because (i) they link atoms with same signs of atomic charges (what is more, these charges are often large, as is the case in highly electronegative oxygen and halogen atoms), (ii) quite often the E or X atom linked by a bond path to another E or X atom is at longer distance than an atom with high positive charge (as B, C and Be) and not linked to the E or X atom by a bond path (see Tables S1 and S2 in Supporting Information).

In the case of point (i), it is worth noting that bond path may occur not only between two atoms with large negative charges (see e.g. E3···E4 in **A1**, where E3=E4=O and its QTAIM/NBO-based atomic charge is −1.23/-0.53 au and **B8**–**B12**, in which there are two such interactions, H6···X3 and
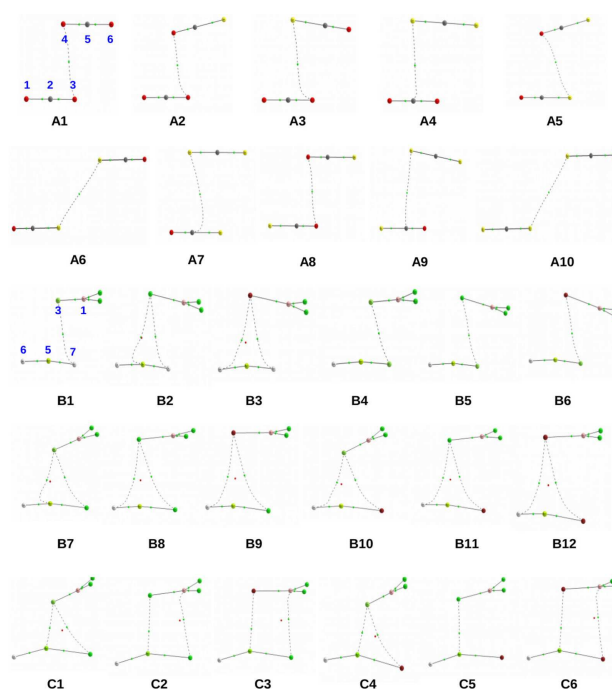

Figure 2. Molecular graphs of the investigated dimers.

E7···X3), but also between two atoms with partial positive charges (e.g. **A4**, **A7** featuring C···S and S···S bond paths, respectively). Adding to this the case of two linked atoms featuring opposite signs of charges (see e.g. **A3** and **C2**), it is obvious that bond path is "blind" to signs of atomic charges. However, atomic charges and clearly negative or positive areas of electrostatic potential should decide on the selection of dominant intermolecular interactions, and therefore also on the dimer structure. Moreover, bond paths are also "blind" to internuclear distances, because they are very often formed between atoms more distant than atoms unconnected by a bond path but the interaction of which should be dominant (Tables S1 and S2).

Let us consider three specific dimers in more detail (Figure 3). In **A2**, i.e. OCO···OCS, a bond path is formed between two oxygen atoms having significantly negative atomic charges (ca. −1.2/−0.5 au), although the distance O···O is longer (3.016 Å) than the distance C···O (2.935 Å) and the carbon atom is highly positive (2.44/1.03 au). This is one of the simple examples showing that, indeed, the presence of bond path does not depend on atomic charges or the internuclear distance. This is even more evident in all **B** systems (except **B7**), which are characterized by the presence of one or even two bond paths connecting negatively charged atoms, whereas the {Be, X} and {E, B} pairs of atoms are not linked by bond paths, although the atoms belonging to each of this pair are much closer to each other and feature opposite signs of their atomic charges. One intermolecular bond path is visible on the molecular graph of **B6** (HBeF···BBrCl₂), namely F···Br. In the light of our discussion, this bond path must be considered as counterintuitive, since both atoms have negative charges (−0.90/−0.87 and −0.55/−0.08 au, respectively), moreover the
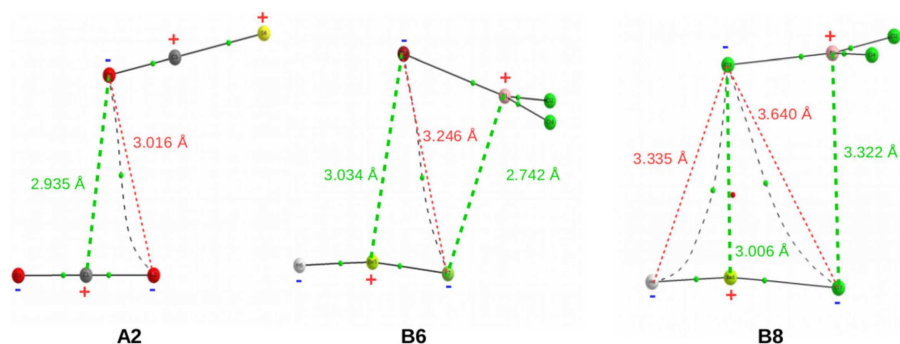
Figure 3. Molecular graphs of **A2**, **B6** and **B8**. The discussed internuclear distances and signs of atomic charges are also shown.
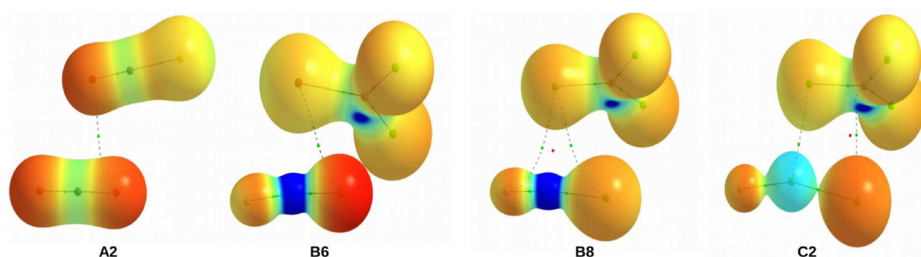

Figure 4. Electrostatic potential maps of OCO···OCS (**A2**), HBeF···BBrCl2 (**B6**), HBeCl···BCl3 (**B8**) and HMgCl···BCl3 (**C2**).

distance between them is greater (3.246 Å) than distances Be···Br (3.034 Å) and F···B (2.742 Å), involving atoms with significant charges (q(Be) = 1.69/1.46 au, q(B) = 1.95/0.25 au) of opposite sign. The molecular graph of **B8** (HBeCl···BCl$_3$) is even more interesting. Namely, despite the relatively small distances Be···Cl (3.006 Å) and Cl···B (3.322 Å), two bond paths are formed, one between the hydridic (i.e. negatively-charged) hydrogen and chlorine, the other between two chlorine atoms.

The analysis of the molecular graphs depicted in Figure 2 shows that intermolecular bond paths are readily formed between highly electronegative atoms, whereas the "reluctance" to boron atom is clearly visible.[28] The former behavior is well known,[22,29,33,43–46,79] while the latter one is in contradiction with the fact that boron atom eagerly creates donor-acceptor triel bonds of various types, e.g. H$^{\delta-}$···B (charge-inverted hydrogen bonds),[76,80–85] N···B,[86] O···B,[87] σ···B,[88] π···B.[89] Therefore, this behavior should be perceived as an obvious manifestation of the uselessness of intermolecular bond paths and an evidence that they do *not* actually show dominant intermolecular interactions.[29]

It should be emphasized that, in addition to the signs and values of atomic charges (which may depend on the method and level of theory), also maps illustrating distribution of electrostatic potential are very valuable tool for indicating potentially most important areas of molecular reactivity and, as a result, dominant intermolecular interactions.[28,29,68–78] Four representative electrostatic potential maps are shown in Figure 4. In the case of the **A2** dimer, the areas of negative electrostatic potential on oxygens and of positive potential on carbons are clearly visible. Considering the mutual orientation of the relevant areas, one should expect that the predominant

dimer stabilizing interactions are C···O rather than O···O. However, the latter of these interactions has its bond path. The fact of the uselessness of intermolecular bond paths is even more clearly shown on the electrostatic potential maps obtained for dimers **B6** and **B8**, where the area of significant positive potential on the boron atom is eye-catching. This is in fact the so-called π-hole.[90] Importantly, the spatial orientation of this hole suggests strong interaction with a nearby halogen atom, on which the negative potential area is clearly visible. It is not surprising then that in these dimers one should expect that the dominant intermolecular interaction should be X···B rather that X···X, especially since the distance of the former is shorter than the latter (Figure 3). Quite similarly, due to the clearly visible area of high electrostatic potential on the beryllium atom, the second expected dominant interaction should be Be···X, which in many cases (Table S2) is even shorter than X···B (or E···B including hydridic hydrogen).

The only formal difference between **C2** and **B8** is that the former of these dimers has magnesium atom instead of beryllium, which, however, completely changes the pattern of intermolecular bond paths. Instead of H···Cl and Cl···Cl as in **B8**, **C2** has Mg···Cl and Cl···B bond paths. It is tempting to explain this difference based on the electrostatic potential maps shown in Figure 4. As for Mg···Cl, then it seems that the only significant difference is the much larger size of the Mg atom (more precisely the contour with $\rho = 0.05$ au) compared to the size of the Be atom. It will be shown that this is crucial. The presence of the Cl···B bond path in **C2** seems to be less understandable (only on the basis of Figure 4), because although the electrostatic potential of Cl in **C2** is more negative than in **B8**, it is even more negative in **B6**, where the F···B bond path is not

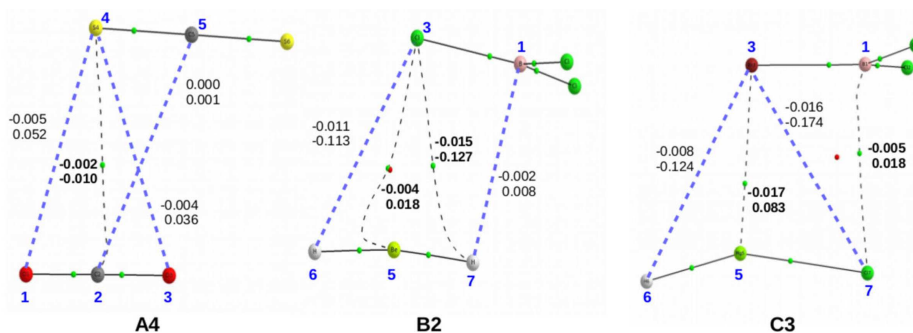**Figure 5.** Values of exchange energy (in au) and α for chosen interactions in dimers **A4**, **B2** and **C3**.

present. What is more, it also does not result from the internuclear distances, because the distance Cl···B in **C2** (3.073 Å) is much longer than F···B in **B6** (2.742 Å). Again, this shows conflict between the suggestion regarding dominant intermolecular interactions obtained from the maps of electrostatic potential and molecular graphs.

3.2. Cause of Presence of Counterintuitive Bond Paths

After presentation of several representative examples showing the problem of the occurrence of counterintuitive bond paths and, what is related to this, the conflict with the suggestion of dominant intermolecular interactions obtained by means of atomic charges and electrostatic potential maps, we are now in place to answer the question of what is the reason for the presence of counterintuitive bond paths. Due to attractiveness of the concept of privileged exchange channels proposed by Pendás et al.,[41] this subsection will start by discussing the results based on this concept. We will show, however, some examples of dimers in which this concept is violated. Next, we will provide a simple explanation of the presence of counterintuitive bond paths based on visual insight into the electron density distribution of a given dimer.[29]

3.2.1. Interaction and Electrostatic Energies

Let us mention here that some interactions traced by bond paths may be characterized by positive values of interatomic IQA-based interaction energies, whereas, quite the opposite, interactions not traced by bond paths may be stabilizing as shown by negative values of interaction energies,[29,43,44,46] i.e. an absence of a bond path does not exclude immediately that a given interaction may be stabilizing. As well as neither the interaction energy nor the electrostatic energy can predict presence or absence of a bond path.[43] These conclusions are also confirmed by our results shown in Tables S3 and S4 in Supporting Information.

3.2.2. Privileged Exchange Channels

As already mentioned, Pendás et al.,[41] have suggested a relationship between the presence of a bond path and the exchange energy. It is worth noting, however, that although in a large number of cases (see Tables S3 and S4) the interaction traced by a bond path is characterized by the highest values of both the exchange energy and the α parameter ($\alpha = E_{ee,xc}^{E_1 E_2} / E_{elst}^{E_1 E_2}$),[43] this conclusion is not true in general. This will be illustrated on the example of three dimers, **A4**, **B2** and **C3** (Figure 5).

In the case of **A4**, interactions O1···S4 and O3···S4 feature larger values of both $E_{ee,xc}^{E_1 E_2}$ and α (−0.005/0.052 and −0.004/ 0.036, respectively) than C2···S4 (−0.002/−0.010) traced by a bond path. In **B2**, although the H7···Cl3 interaction, which has a bond path, features the highest values of $E_{ee,xc}^{E_1 E_2}$ and α (−0.015 au and −0.127, respectively), these values are quite low (-0.004 au and 0.018, respectively) for Be5···Cl3, which also features bond path, and more importantly they are lower than for H6···Cl3 (−0.011 au, −0.113, respectively), which, however, does not have a bond path. Similar situation occurs, e.g., in the **C3** dimer. The Cl7···B1 contact is characterized by relatively small values of both parameters (−0.005/0.018), but has a bond path, whereas, e.g., interaction Cl7···Br3, for which the value of $E_{ee,xc}^{E_1 E_2}$ (−0.016 au) is comparable to the value (−0.017 au) for the Mg5···Br3 interaction (traced by a bond path) and α is clearly the largest (−0.174), such a bond path does not appear. Thus, the presence of a bond path is not determined by large or maximum values of the exchange energy[41] or the α parameter, because, as shown, interactions characterized by large or even maximum values of $E_{ee,xc}^{E_1 E_2}$ and α very often do not feature bond paths.

So what factor determines the presence of bond path for this rather than another interaction? According to the concept of privileged exchange channels proposed by Pendás et al. we learn that: "The existence or absence of a BP is related to the competition of different exchange channels…".[41] This is to mean that a given atom creates a bond path to that atom that will provide the highest energetical gain due to electron spin pairing. However, we will soon show that this concept is *not* correct.

3.2.3. Concept of Secondary Interactions

To capture the concept of Pendás et al. in a quantitative way, Tognetti and Joubert have introduced the concept of secondary interactions (next to the primary one, which is simply the interaction we are just interested in). They have been defined as "interactions between one of the atoms considered in the primary interaction and an atom directly bonded (by a BP) with the second atom involved in the primary interaction".[43] Then, by examining the causes of bond paths for intramolecular interactions O···X (X=O, S, a halogen atom), Tognetti and Joubert have shown that they are present on molecular graphs when $\beta > 1.59$, while they are absent when $\beta < 1.35$,[43] where β is the ratio of the exchange energy of the primary interaction ($E_{ee,xc}^{E_1E_2}$) and the maximum value of the exchange energy of all the secondary interactions ($E_{ee,xc}^{E_1E_2}(\text{sec.})^{max}$):

$$\beta = E_{ee,xc}^{E_1E_2} / E_{ee,xc}^{E_1E_2}(\text{sec.})^{max}. \tag{5}$$

In spite of more or less subtle differences in geometry, a common feature of all the analyzed dimers is a nearly parallel arrangement of interacting monomers (see Figure 1). It allows for their simplified graphical representation, as in Figures 6–8, which show the values of exchange energy for all nine unique intermolecular primary (brown line) and their secondary (brown dashed line) interactions. The calculated values of β are also
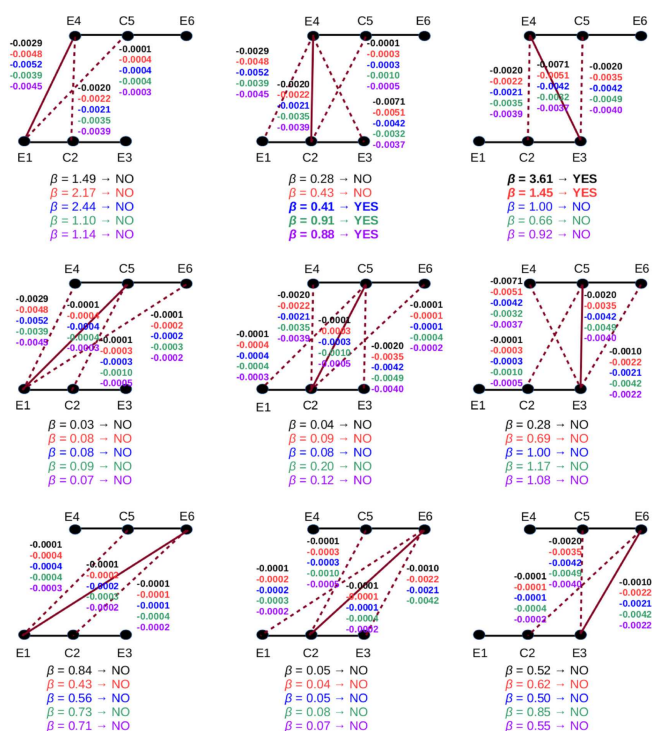

Figure 7. Values of exchange energy (in au) for all unique intermolecular primary (brown line) and secondary (brown dashed line) interactions in **B1** (black), **B2** (red), **B3** (blue) and **B7** (green) (E=H in **B1**-**B3** and F in **B7**; X=F in **B1** and **B7**, Cl in **B2**, Br in **B3**). For each primary interaction, also the determined value of β (eq. 5) and information whether this interaction has a bond path (see also Figure 2) are given.

given together with information on whether the given interaction creates a bond path (see also Table 1).

The **A2** dimer is a typical one that meets the concept of the privileged exchange channels both qualitatively and quantitatively. As one can see (Figure 6), from among all the primary interactions, O3···O4 is clearly distinguished by the highest value of β (3.61 vs 0.03−1.49), and indeed only this interaction has a bond path. It is enough, however, to go to **A3** to see that β calculated for E3···E4 (i.e. O3···S4) drops to 1.45, i.e. it falls into the transition zone given by Tognetti and Joubert (1.35−1.59), in which both the interactions that had a bond path and those that did not have such a path were found.[43] Other interactions that meet the concept of privileged exchange channels and inequalities of Tognetti and Joubert are (Figure 7), e.g. H7···F3 in **B1** ($\beta = 4.57$) and both H7···Br3 and H6···Br3 in **B3** (2.92 and 2.34, respectively).

Although both the concept of privileged exchange channels proposed by Pendás et al.[41] and the quantitative attempt to explain the presence or absence of bond path using parameter β introduced by Tognetti and Joubert[43] are confirmed in many cases, we are now proceeding to present exemplary interactions in which both these concepts are violated. These results show, therefore, that both these concepts are incorrect or at least still incomplete.
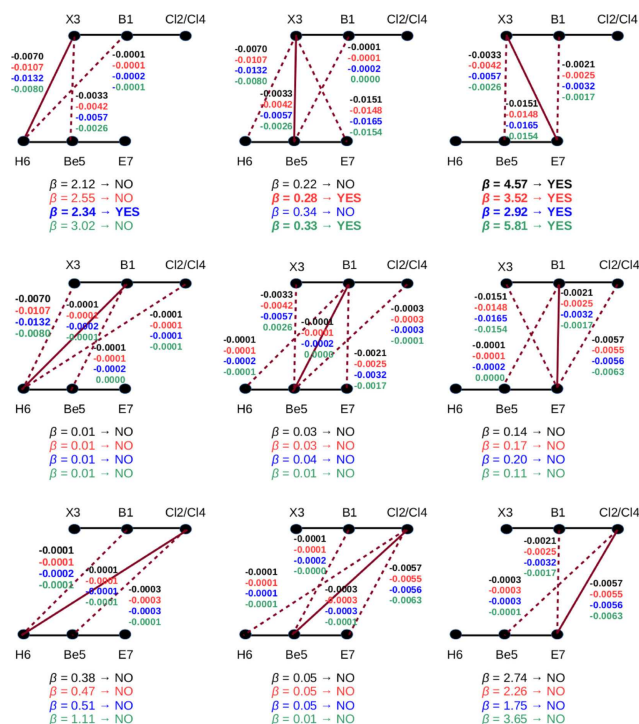

Figure 6. Values of exchange energy (in au) for all unique intermolecular primary (brown line) and secondary (brown dashed line) interactions in **A2** (black), **A3** (red), **A4** (blue), **A7** (green) and **A9** (violet) (E is either O or S). For each primary interaction, also the determined value of β (eq. 5) and information whether this interaction has a bond path (see also Figure 2) are given.
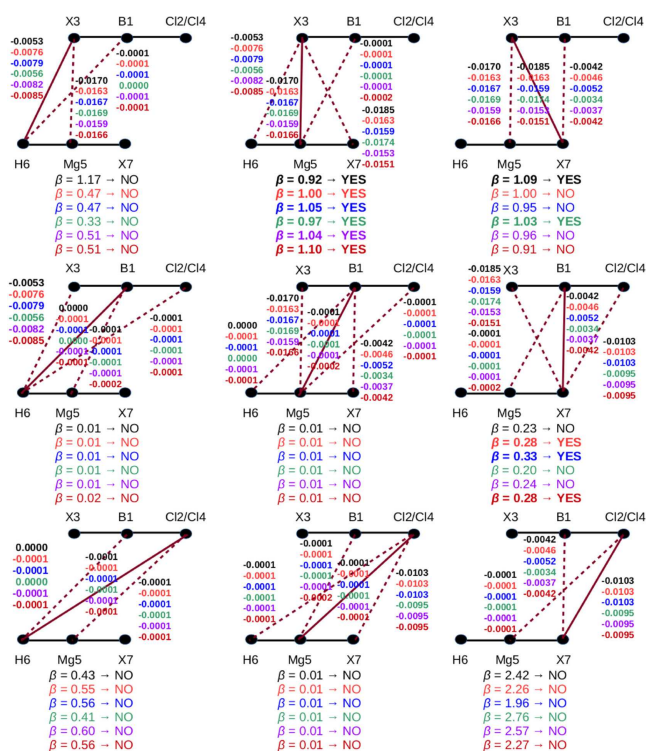
Figure 8. Values of exchange energy (in au) for all unique intermolecular primary (brown line) and secondary (brown dashed line) interactions in **C1** (black), **C2** (red), **C3** (blue), **C4** (green), **C5** (violet) and **C6** (brown) (X7 = Cl in **C1**–**C3** and Br in **C4**–**C6**; X3 = F in **C1** and **C4**, Cl in **C2** and **C5**, Br in **C3** and **C6**). For each primary interaction, also the determined value of β (eq. 5) and information whether this interaction has a bond path (see also Figure 2) are given.

Table 1. Value of β for chosen primary interactions.

Dimer	Prim. int.	Sec. int.	β	BP
A2	O3···O4	O3···C5	3.61	YES
A3	O3···S4	O3···C5	1.45	YES
A4	C2···S4	O1···S4	0.41	YES
A7	C2···S4	O1···S4	0.91	YES
A9	C2···S4	S1···S4	0.88	YES
B1	H7···F3	Be5···F3	4.57	YES
	H7···Cl2	H7···B1	2.74	NO
B2	H7···Cl3	Be5···Cl3	3.52	YES
	Be5···Cl3	H7···Cl3	0.28	YES
	H6···Cl3	Be5···Cl3	2.55	NO
B3	H7···Br3	Be5···Br3	2.92	YES
	H6···Br3	Be5···Br3	2.34	YES
B7	Cl7···F3	Be5···F3	5.81	YES
	Be5···F3	Cl7···F3	0.33	YES
	Cl7···Cl2	Cl7···B1	3.65	NO
	H6···F3	Be5···F3	3.02	NO
C1	Mg5···F3	Cl7···F3	0.92	YES
	Cl7···F3	Mg5···F3	1.09	YES
	Cl7···Cl4	Cl7···B1	2.42	NO
C2	Mg5···Cl3	Cl7···Cl3	1.00	YES
	Cl7···Cl3	Mg5···Cl3	1.00	NO
	Cl7···B1	Cl7···Cl4	0.28	YES
	Cl7···Cl4	Cl7···B1	2.26	NO
C3	Mg5···Br3	Cl7···Br3	1.05	YES
	Cl7···Br3	Mg5···Br3	0.95	NO
	Cl7···B1	Cl7···Br3	0.33	YES
	Cl7···Cl2	Cl7···B1	1.96	NO
C4	Mg5···F3	Br7···F3	0.97	YES
	Br7···F3	Mg5···F3	1.03	YES
	Br7···Cl2	Br7···B1	2.76	NO
C5	Mg5···Cl3	Br7···Cl3	1.04	YES
	Br7···Cl3	Mg5···Cl3	0.96	NO
	Br7···Cl2	Br7···B1	2.57	NO
C6	Mg5···Br3	Br7···Br3	1.10	YES
	Br7···Br3	Mg5···Br3	0.91	NO
	Br7···B1	Br7···Br3	0.28	YES
	Br7···Cl2	Br7···B1	2.27	NO

3.2.4. Violation of the Concepts of Privileged Exchange Channels and Secondary Interactions

What is particularly both interesting and important, our research has revealed the presence of many interactions that feature, admittedly, a bond path and yet do *not* meet the concept of the privileged exchange channels by Pendás et al.[41] or the inequalities given by Tognetti and Joubert.[43] This is the first such report.

In the case of dimers **A** shown in Figure 6, the β values calculated for C2···S4 in **A7**, **A9** and **A4** are respectively 0.91, 0.88 and 0.41. In the last of these cases, the exchange energy for the C2···S4 (primary) interaction having BP is −0.0021 au, while these values are respectively −0.0052 and −0.0042 for O1···S4 and O3···S4. Even lower values of β have been found in **B2** and **B7** as well as some **C**-type dimers, in which the intermolecular interactions having corresponding bond paths are generally characterized by low β values (Figure 8). In the case of **B2** and **B7** (Figure 7), these very small values of β (0.28 and 0.33, respectively) refer to the Be5···X3 interaction (X=Cl and F, respectively), which together with E7···X3 (E=H and Cl, respectively) has a bond path (however for the latter of these interactions, the β values are very large: 3.52 and 5.81, respectively). In terms of low values of β, the **C**-type dimers shown in Figure 8 deserve particular attention, since in this case

all intermolecular bond paths are characterized by β values close to one, and additionally, **C2**, **C3** and **C6** dimers also have bond paths for the X7···B1 (X=Cl in **C2** and **C3**, and Br in **C6**) interaction, for which β amounts to ca. 0.3 only. This is due to the near presence of the X7···X3 interaction, for which the value of the exchange energy is significant and, more importantly, at the same time either close to the value for Mg5···X3 or higher than for X7···B1.

In addition to this spectacular evidence of the violation of the concept of privileged exchange channels, it is also worth noting that the dimers shown have many interactions without corresponding bond paths, although their β values are significant, much higher than the value of 1.59 determined by Tognetti and Joubert.[43] See (Table 1) for example Cl7···Cl2/Cl4 and H6···F3 (3.65 and 3.02, respectively) in **B7** or H7···Cl2/Cl4 (2.74) and Br7···Cl2/Cl4 (2.76) in **B1** and **C4**, respectively. Of course, the cases of small β values for both the Be5···X3 interaction in **B2** and **B7** and the X7···B1 interaction in **C2**, **C3** and **C6** are particularly striking.

In the light of the results presented, we conclude that either the bond path has nothing to do with both the concept of privileged exchange channel proposed by Pendás et al.[41] and of secondary interactions and inequalities for β introduced by Tognetti and Joubert[43] or these both concepts need to be
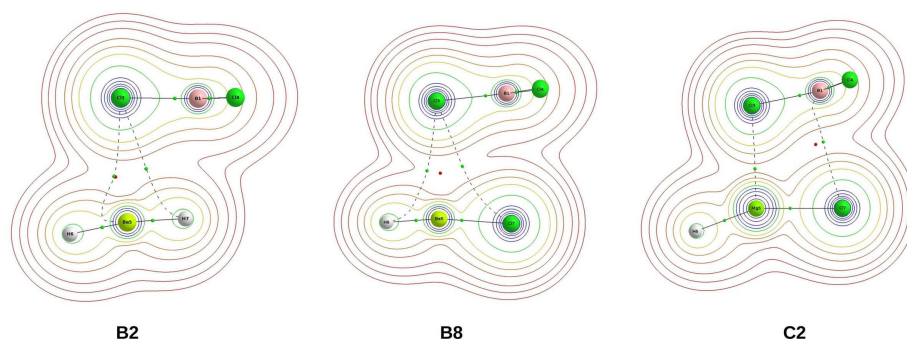
Figure 9. Isodensity contour (red – 0.0 au, yellow – 0.1 au, green – 0.2 au, cyan – 0.3 au, blue – 0.4 au) plots for **B2**, **B8** and **C2**.

revised and completed by the case of intermolecular interactions. It seems that the most probable reason for the described violation of both these concepts is the fact that the interatomic exchange energy, $E_{ee,xc}^{E_1 E_2}$, and a bond path come from other worlds. Namely, the former is derived by the partitioning of the second order reduced density matrix and, morover, then integrating the entire areas of basins E_1 and E_2.[51] Therefore, in this sense, $E_{ee,xc}^{E_1 E_2}$ is a global parameter. Bond path, on the other hand, is a local quantity, because it is obtained by determining the electron density gradient at a point. Why, then, as Pendás et al. have suggested,[41] would the relationship between $E_{ee,xc}^{E_1 E_2}$ and bond path exist at all?

3.2.5. Visual Insight Into the Distribution of Electron Density

First of all, it should be noted that bond path is simply a case (but particular) of the electron density gradient line, and thus can be obtained by continuously progressing determination of the electron density gradient vector starting from BCP. That is why BP can be referred to as a line of maximum density, linking atomic nuclei.[1,4,5] Therefore, it is not surprising that the vector penetrates areas with high electron density and avoids those in which the electron density is locally lower. For the same reason, the gradient vector directs itself towards the region where the distribution of the electron charge is particularly expanded and, quite the contrary, it is completely blind to the areas where distributions of the electron charge are spatially compressed.[29] This behavior of the gradient vector is universal and is particularly evident in cases where the gradient vector approaches a pair of atoms with significantly different sizes of isodensity contours, i.e. areas characterized by the same values of the electron density. This may happen, for example, in the case of Be—X and B—X bonds, where X is a halogen atom. It is worth noting that if X is strongly electronegative (and in addition there are more such atoms, as in, e.g., BX₃), the B atom (or Be) will get a large positive charge and X negative. It is therefore clear why bond path very often links two strongly electronegative atoms, as, e.g., in X⋯X, X⋯O or O⋯O.[22,23] As it has already been shown, this does not mean that these interactions are stabilizing or even dominant. Quite the contrary, interactions of type X⋯B, O⋯B, etc. should be

dominant due to the domination of long-range electrostatics, however, they are not usually associated with the presence of bond paths.

The behavior of a bond path at the proximity of two atoms with clearly different degrees of electron charge distribution is well seen, e.g. in the **B8** dimer. Figure 9 shows the molecular graph of this dimer together with the isodensity contour. Similar contours were also determined for comparison purposes for **B2** and **C2**. Starting from the BCP of H6⋯Cl3 towards the HBeCl molecule, we can see that the gradient vector of the electron density is moving towards the hydridic hydrogen with a slightly more expanded charge distribution and not to the more compressed beryllium atom. This completely natural behavior of the gradient vector is even more evident in the case of Cl7⋯Cl3. Due to the larger size of the Cl7 atom compared to the previously discussed H6 (and of course also Be5), the gradient vector, starting its journey at BCP, almost immediately sees Cl7 and monotonously directs towards its nucleus. If the route in the opposite direction is considered instead then, again, the gradient vector (which in fact is already close to Cl) finds highly expanded chlorine atom instead of much compressed boron. It is symptomatic that this completely natural behavior of the electron density gradient vector leads to counterintuitive bond paths.

Taking into account the topological explanation of the presence of the H6⋯Cl3 and Cl7⋯Cl3 bond paths in **B8**, the presence of the Be5⋯Cl3 bond path in the similar **B2** dimer may now seem quite surprising. However, the subtle difference in geometries of both these dimers causes the BCP of the Be5⋯Cl3 interaction to be somewhat closer to the beryllium atom and the electron density gradient vector going towards the H6-Be5 bond now finds, somewhat incidentally, the beryllium atom. The somewhat accidental origin of this event is evidenced by the much smaller distance between the BCP of this interaction and the ring critical point (RCP) than in the **B8** dimer.

Comparing the isodensity contours for **B8** and **C2**, it is clearly seen that in the latter case the electron density gradient vector easily finds the magnesium atom. It results mainly from the escape of the hydridic hydrogen from the Mg—Cl axis and therefore its much greater remoteness than in **B8**, but also from much more expanded charge distribution of Mg in **C2** comparing to Be in **B8**. The presence of the Cl7⋯B1 bond path

in **C2** appears to result from a much flatter electron density region in the intermolecular area than it does in the **B8** dimer. For this reason, a negative gradient vector leading from the Cl7 atom towards the BCl_3 molecule is not drawn into regions close to Cl3, as is the case in **B8**. Note that the RCP-RCP distance is small and the BCP of Cl7···B1 is characterized by a fairly large bond ellipticity, amounting to 3.0.

3.3. Dominant Intermolecular Interactions

The discussed examples sufficiently show that, in general case, the bond path connecting more distant atoms, which occurs, e.g. in dimers, has nothing in common with dominant intermolecular interactions. Dominant intermolecular interactions should therefore be guessed utilizing other than topological means, in particular those based on electrostatic effects. Maps illustrating distribution of electrostatic potential seem to be a proper choice. As already mentioned, such maps are often used to show most probable areas of intermolecular contacts.[68–78] Therefore, structures of many molecular systems, including various dimers, can be explained by a simple electrostatic reasoning. Interpretation of intermolecular (as well as many intramolecular) bond paths as evidence of the presence of dominant interactions is often incorrect. Of course, this conclusion does not apply to all possible cases. It is easy to imagine e.g. a linear dimer A—B···C—D, in which the bond path B···C must indicate the dominant intermolecular interaction just because the B···C distance is definitely the shortest among all the intermolecular distances. On the other hand, however, this bond path must be present on the molecular graph of this dimer to fulfil the Poincaré-Hopf relationship.[25]

4. Conclusions

In this article, we answered the question, what indicates that the given interaction between distant atoms is the dominant one among many others. Unfortunately, the still widespread opinion, based on orthodox QTAIM, is that the dominant interaction is indicated by the presence of a bond path on molecular graph of the considered system. However, contrary to this opinion, we have shown that in general bond paths have nothing in common with dominant interactions between distant atoms. Moreover, bond paths are blind to both signs of atomic charges and intermolecular distances. Therefore, we concluded that bond paths between distant atoms are generally useless. As a consequence, the dominant intermolecular (any many intramolecular) interactions should not be evidenced by bond paths. Quite the opposite, a reliable picture of dominant intermolecular interactions can be obtained using e.g. maps of electrostatic potential. It is shown that such maps perfectly explain the mutual orientation of interacting molecules in a dimer. Our statement fully justifies Shahbazian's suggestion to remove the misleading "bond" term from expressions such as bond path and bond critical point.

We have shown for the first time that many interactions admittedly featuring a bond path violate both the concept of privileged exchange channels proposed by Pendás and his collaborators and the inequalities introduced by Tognetti and Joubert for parameter β based on the so-called secondary interactions. Namely, in some cases a bond path is formed, although the interaction traced by this bond path in *not* associated with the privileged exchange channel. Furthermore, many intermolecular interactions do not feature bond paths, although β values determined for them are very large. Therefore, it is seems that bond path has nothing in common with both the concept of privileged exchange channels and the inequalities for β. We have suggested that the cause of this observed violation may be other sources of the A—B interatomic exchange energy and bond path. Namely, the former quantity is global, whereas the latter one is local.

We have also proposed a very simple but illustrative explanation of the frequently observed fact that bond paths very often occur against chemical intuition regarding dominant interatomic interactions. In this case, these bond paths may be called counterintuitive, because their presence contradicts other characteristics of the system. Very often such bond path connect atoms with same signs of atomic charges, in particular in the case of highly electronegative halogen atoms with much expanded charge distributions. Moreover, the distance between such atoms is often much larger than the distance between atoms with clearly opposite signs of atomic charges or belonging to areas whose strong interaction is suggested by the appropriate distribution of electrostatic potential, but the atoms are not linked by a bond path. We have shown that such counterintuitive bond paths result from the quite natural behavior of the electron density gradient vector forming this path. This behavior consists in searching for areas with maximum electron density and avoiding areas of low value. The universality of this principle is best illustrated when the electron density gradient vector approaches a pair of atoms with significantly different sizes of isodensity contours, as is the case, e.g. in Be—X or B—X bonds. It is quite symptomatic that counterintuitive bond paths result from completely natural behavior of the electron density gradient vector forming a bond path.

Conflict of Interest

The authors declare no conflict of interest.

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