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# An Analysis of Substituent Effects in Ethane Derivatives: The Quantum Theory of Atoms in Molecules Approach

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MP2/6-311++G(d,p) calculations were performed on ethane and its simple derivatives. Different substituents such as: Li, Na, BeH, $BH_2$, OH, $NH_2$, F and $NO_2$ were considered. The mono- and disubstituted derivatives of ethane were analyzed. The quantum theory of "atoms in molecules" was applied to localize bond critical points and to analyze relationships between their locations and characteristics of the species. The numerous correlations were found showing the crucial influence of substituent effects. It was also revealed that such parameters as the carbon−carbon distance, or the electron density at C−C bond critical point do not show the systematic changes caused by substituent effects. This means that some of QTAIM parameters, especially the positions of BCPs may be useful to detect numerous sensitive effects if the latter ones do not affect the traditionally analyzed geometrical parameters of a molecule, such as bond lengths.

## Introduction

It is well-known that the quantum theory of "atoms in molecules" (QTAM)[1] is a useful tool to analyze different intra- and intermolecular interactions.[1,2] If any pair of attractors attributed to nuclei is connected by the bond path (BP) thus the point characterized by the minimum of the electron density on that path is called the bond critical point (BCP). The characteristics of BCP often indicate the specific type of interactions between this pair of atoms. There are closed-shell interactions such as ionic bonds, van der Waals interactions and hydrogen bonds; and in addition there are also the shared interactions such as covalent bonds. The following topological QTAIM parameters characterize any BCP considered and hence further any pair of interacting atoms corresponding to this BCP: the electron density at BCP ($\rho_C$), its laplacian ($\nabla^2\rho_C$), the elipticity concerning the pair of interacting atoms ($\varepsilon$), the parallel and the perpendicular curvatures of $\rho_C$ to the BP direction ($\lambda_1$, $\lambda_2$, $\lambda_3$), the total electron energy density at BCP ($H_C$), and components of the latter one—the kinetic electron energy density ($G_C$) and the potential electron energy density ($V_C$).[1,2] The mentioned characteristics could classify any type of interaction not only the mentioned here classes. In addition, topological parameters allow to characterize the considered interaction in detail. Hence, for example, it is possible to evaluate if hydrogen bonding is the weak interaction similar in nature to the van der Waals one or it is a very strong interaction and it may be classified as hydrogen bonding possessing features of the covalent bond.[3]

The numerous correlations were found for closed-shell interactions between geometrical, energetic and topological parameters.[4] For example, the relationship between the atom-atom distance and the electron density at the corresponding BCP is very well-known.[5] This dependence is exponential for the broad range of distances and it reflects the nature of interactions often described by exponential functions.[6]

However, the linear correlations are usually observed for the shorter ranges of distances. For example, the well linear correlation was found between the ring bond length of benzenoid hydrocarbons and the electron density at the corresponding BCP.[7] However such dependencies are hardly detected. In addition, they are usually established only for the narrow ranges of distances corresponding to bond lengths. It seems that the considered interactions should belong to the homogeneous sample of analyzed species.[8] Similar correlations were found for the relationships between distance and the mentioned above topological parameters such as $H_C$, $V_C$, and $G_C$.[9] The various relationships between geometrical, energetic and QTAIM parameters were analyzed by Espinosa and co-workers.[10] The authors have also analyzed correlations related to curvatures of $\rho_C$ to the BP ($\lambda$-values). Very recently dependencies between the QTAIM characteristics and the components of the decomposition of the interaction energy were found revealing that both classes of parameters may be useful to describe the nature of interactions, for example to indicate if any hydrogen bonding is covalent in nature, medium in strength or it should be rather classified as van der Waals interaction.[11]

There are also the studies on ring critical point (RCP) since numerous correlations were found between various energetic and geometrical parameters and characteristics of RCP.[12,13] The ring critical point is created if there is the "closed ring" of interacting atoms. The numerous correlations were found between characteristics of RCP and the parameters describing the strength of intramolecular hydrogen bonding. The similar relations were found for RCP existing in the ring created by two hydrogen bonds connecting carboxylic groups and the covalent bonds of these groups.[14] Interestingly, innovative dependencies were analyzed recently for cage critical point (CCP).[15]

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It is worth to mention that the dependencies and correlations described briefly above relate usually to the nonbonding interactions and the number of studies concerning covalent bonds is rather restricted. For example, in one of the first QTAIM studies the correlation between CC bond length and the electron density at the corresponding BCP in ethane, ethane, and benzene was observed.[1c] Similar distance−electron density at BCP dependencies were analyzed for the electron density found experimentally[16] as well as that one corresponding to the calculated wave function.[7,17]

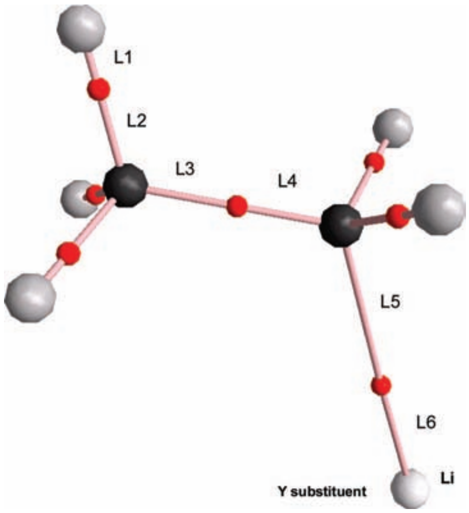
The goal of this study is to analyze substituent effects for the ethane derivatives. The studies on substituent effects for such systems (one may call them $\sigma$-electron ones), are rather rare. However, numerous investigations were carried out for the $\pi$-electron systems, mostly cyclic ones, like for example benzene derivatives. One of the often applied definitions of the substituent effect takes into account the division of the system into three parts:[18,19] the substituent (X) which is changed, the functional group (Y) which is considered as being influenced by X and the transmitting part of the system. The latter one is usually the benzene ring but the other types of transmitting moieties were also considered, such as for example naphthalene.[20] There are the other ways to define the substituent effect [21,22] but mainly these definitions refer to the $\pi$-electronic systems, very often the aromatic ones. In the latter case the interrelations between the aromaticity and the substituent effect are the subject of investigations.[23]

There are the other numerous studies related to the substituent effect, for example, dependencies between the substituent properties and the bond lengths and valence bond angles were detected for benzene derivatives and so-called additivity rules were proposed.[24−26] The aromaticity indexes were proposed to describe the cyclic $\pi$-electron compounds. One can mention the HOMA index[27] often applied to describe aromatic systems, and more general the physicochemical properties of cyclic compounds. The substituent effects were also analyzed in acetylene[28] and ethylene derivatives.[29] However correlations between the geometry of the latter species and the substituent properties have not been found. There are no correlations between the CC bond length and characteristics of substituents, no correlations between C═C bond length in ethylenes (or C≡C in acetylenes) and the electron density at the corresponding BCP or its laplacian. It is very interesting that for acetylenes and ethylenes the CC bond length is rather insensitive to the substituent attached. However dramatic differences in positions of CC bond critical point were observed for these species if different substituents are taken into account.[28,29] These dramatic changes of BCP position may be attributed to $\pi$-electrons of those species. Hence it seems to be interesting to investigate if such meaningful changes are observed for "non-$\pi$-electron systems" as for example for simple derivatives of ethane. It is interesting to establish if the BCP position may be useful as an additional characteristic of substituent or of the other physicochemical properties of analyzed system. We believe that the position of critical point may be a descriptor of a given property of analyzed systems. For example, relationships between the RCP position within benzene ring and the hydrogen bond strength were analyzed recently for complexes of methoxybenzene with the simple Lewis acids.[30]

## Computational Details

The calculations on ethane and its derivatives were carried out by the use of Gaussian 03 set of codes.[31] Geometries of molecules were fully optimized at MP2/6-311++G(d,p) level of theory. Compounds of a general formula Y−CH$_2$−CH$_2$−X were considered. X and Y designate simple substituents such as: H, F, Li, Na, OH, BeH, NH$_2$, BH$_2$, and NO$_2$. Hence three series of species were analyzed, those with H-atom as Y-substituent and different X-substituents, those with Y = F, and the last series where Y = Li. Scheme 1 presents the ethane derivative where there is no X-substituent (X = H). Since Y = Li, this species thus (Scheme 1) belongs to the third series of compounds. Additionally, the scheme defines distances between bond critical points (BCPs) and the corresponding attractors attributed to the nuclei (L1−L6 values). It is worth to mention that mono- and disubstituted derivatives of ethane are considered. If two substituents exist thus each one is attached to the other carbon atom. Since for such disubstituted ethanes different conformations may exist (corresponding to different local minima) thus the conformer corresponding to the lowest energy is taken into account. For the considered derivative of ethane it is usually the conformation where substituents are positioned at the opposite sides thus their distance is the greatest one (*trans*-conformation).

SCHEME 1



The electron densities corresponding to MP2/6-311++(d,p) wave functions were applied for QTAIM calculations.[1] The QTAIM theory was applied to find bond critical points (BCPs) and to characterize them in terms of electron densities and their Laplacians. The localization of BCPs was also analyzed. The QTAIM calculations were performed with the use of AIM2000 program.[32]

## Results and Discussion

Tables 1−3 present the selected parameters of the ethane derivatives considered here. There are the C−C bond lengths, *R*, and the electron densities at the corresponding BCPs. Tables 1−3 include also the laplacians of the electron density for those BCPs. The L1-L6 values, (atoms' radii), collected in the tables describe the BCPs' positions, starting from the X-substituents and terminated at the Y-ones. Scheme 1 describes appropriately the meaning of L-values. For example, L1 designates the radius of the substituent atom directed to the carbon atom of the central C−C bond.

Tables 1−3 also include the mean values of the mentioned above values as well as their variances. The data in all three tables show the similar tendencies for the species analyzed. There is a small variance of the C−C bond length, (of the order of $10^{-4}$), the variance of the electron density at C−C BCP is of

**TABLE 1: Selected Geometrical (in Å) and Topological (in au) Parameters of Ethane Derivatives, Y = H, with the Designations According to Scheme 1**

| X | $R$ | $\rho$ | $\nabla^2\rho$ | L1 | L2 | L3 | L4 | L5 | L6 |
|---|---|---|---|---|---|---|---|---|---|
| H | 1.529 | 0.240 | −0.557 | 0.384 | 0.695 | 0.765 | 0.765 | 0.695 | 0.384 |
| F | 1.512 | 0.256 | −0.643 | 0.931 | 0.467 | 0.775 | 0.737 | 0.697 | 0.383 |
| Li | 1.545 | 0.227 | −0.480 | 0.704 | 1.310 | 0.746 | 0.798 | 0.695 | 0.392 |
| Na | 1.536 | 0.231 | −0.500 | 1.011 | 1.363 | 0.747 | 0.789 | 0.697 | 0.392 |
| OH | 1.521 | 0.250 | −0.608 | 0.936 | 0.490 | 0.766 | 0.755 | 0.697 | 0.383 |
| BeH | 1.546 | 0.227 | −0.482 | 0.566 | 1.128 | 0.765 | 0.781 | 0.697 | 0.384 |
| $NH_2$ | 1.523 | 0.247 | −0.593 | 0.879 | 0.588 | 0.768 | 0.755 | 0.696 | 0.384 |
| $BH_2$ | 1.533 | 0.236 | −0.536 | 0.513 | 1.050 | 0.766 | 0.767 | 0.696 | 0.384 |
| $NO_2$ | 1.520 | 0.245 | −0.585 | 0.934 | 0.566 | 0.789 | 0.731 | 0.699 | 0.379 |
| var[a] | $1.35 \times 10^{-4}$ | $1.08 \times 10^{-4}$ | $3.40 \times 10^{-3}$ | 0.051 | 0.130 | $1.71 \times 10^{-4}$ | $5.07 \times 10^{-4}$ | $1.53 \times 10^{-6}$ | $1.83 \times 10^{-5}$ |
| mean | 1.529 | 0.240 | −0.554 | 0.762 | 0.851 | 0.765 | 0.764 | 0.697 | 0.385 |

[a] Variance.

**TABLE 2: Selected Geometrical (in Å) and Topological (in au) Parameters of Ethane Derivatives, Y = F, with the Designations According to Scheme 1**

| X | $R$ | $\rho$ | $\nabla^2\rho$ | L1 | L2 | L3 | L4 | L5 | L6 |
|---|---|---|---|---|---|---|---|---|---|
| H | 1.512 | 0.256 | −0.643 | 0.383 | 0.697 | 0.737 | 0.775 | 0.467 | 0.931 |
| F | 1.516 | 0.263 | −0.691 | 0.928 | 0.463 | 0.758 | 0.758 | 0.463 | 0.928 |
| Li | 1.491 | 0.258 | −0.628 | 0.707 | 1.307 | 0.703 | 0.788 | 0.497 | 0.940 |
| Na | 1.485 | 0.262 | −0.643 | 1.011 | 1.359 | 0.702 | 0.783 | 0.505 | 0.939 |
| OH | 1.520 | 0.260 | −0.666 | 0.934 | 0.488 | 0.747 | 0.773 | 0.464 | 0.929 |
| BeH | 1.511 | 0.250 | −0.595 | 0.569 | 1.130 | 0.731 | 0.779 | 0.473 | 0.933 |
| $NH_2$ | 1.518 | 0.258 | −0.658 | 0.876 | 0.589 | 0.745 | 0.773 | 0.464 | 0.931 |
| $BH_2$ | 1.512 | 0.255 | −0.629 | 0.514 | 1.053 | 0.736 | 0.776 | 0.468 | 0.932 |
| $NO_2$ | 1.522 | 0.254 | −0.635 | 0.930 | 0.564 | 0.771 | 0.751 | 0.463 | 0.925 |
| var[a] | $1.67 \times 10^{-4}$ | $1.68 \times 10^{-5}$ | $7.31 \times 10^{-4}$ | 0.0507 | 0.130 | $5.22 \times 10^{-4}$ | $1.35 \times 10^{-4}$ | $2.52 \times 10^{-4}$ | $2.37 \times 10^{-5}$ |
| mean | 1.510 | 0.257 | −0.643 | 0.761 | 0.850 | 0.737 | 0.773 | 0.474 | 0.932 |

[a] Variance.

**TABLE 3: Selected Geometrical (in Å) and Topological (in au) Parameters of Ethane Derivatives, Y = Li, with the Designations According to Scheme 1**

| X | $R$ | $\rho$ | $\nabla^2\rho$ | L1 | L2 | L3 | L4 | L5 | L6 |
|---|---|---|---|---|---|---|---|---|---|
| H | 1.545 | 0.227 | −0.480 | 0.392 | 0.695 | 0.798 | 0.746 | 1.310 | 0.704 |
| F | 1.491 | 0.258 | −0.628 | 0.940 | 0.497 | 0.788 | 0.703 | 1.307 | 0.707 |
| Li | 1.565 | 0.215 | −0.387 | 0.702 | 1.238 | 0.783 | 0.783 | 1.238 | 0.702 |
| Na | 1.553 | 0.220 | −0.414 | 1.007 | 1.316 | 0.780 | 0.763 | 1.244 | 0.702 |
| OH | 1.512 | 0.248 | −0.572 | 0.939 | 0.510 | 0.786 | 0.726 | 1.309 | 0.707 |
| BeH | 1.590 | 0.203 | −0.328 | 0.568 | 1.096 | 0.807 | 0.782 | 1.235 | 0.697 |
| $NH_2$ | 1.529 | 0.239 | −0.526 | 0.887 | 0.596 | 0.787 | 0.743 | 1.314 | 0.708 |
| $BH_2$ | 1.549 | 0.224 | −0.461 | 0.516 | 1.049 | 0.800 | 0.749 | 1.325 | 0.709 |
| $NO_2$ | 1.511 | 0.241 | −0.538 | 0.944 | 0.575 | 0.809 | 0.702 | 1.308 | 0.707 |
| var[a] | $9.40 \times 10^{-4}$ | $3.01 \times 10^{-4}$ | $9.04 \times 10^{-3}$ | 0.0513 | 0.1089 | $1.13 \times 10^{-4}$ | $8.91 \times 10^{-4}$ | $1.37 \times 10^{-3}$ | $1.49 \times 10^{-5}$ |
| mean | 1.538 | 0.231 | −0.482 | 0.766 | 0.841 | 0.793 | 0.744 | 1.288 | 0.705 |

[a] Variance.

the same order, even for the subsample with Y = F it is of about $\sim 10^{-5}$. One can see the similar tendencies for laplacian of the electron density at C−C BCP, only for the Y = Li subsample the order has an approximate value of $\sim 10^{-3}$. As concerns the L-values, only for L1 and L2 variances are meaningful while for the other L-values there is the same order of variance ($\sim 10^{-4}$) as for the bond length, electron density and laplacian. Only very low value of variance ($10^{-5}$) is predicted for L6.

The values of variances for L-values may be explained in the following way. L6 for subsamples does not change since it is related to the radius of Y-atom substituent, H, F, and Li, respectively. It means that the other X-substituents do not influence in any substantial way, Y and particularly C−Y bond since they interact through C−C single bonds which do not transfer the X-properties. The C−Y bond length is insensitive to X-substituent effect since L5 is also characterized by low values of variances (C−Y bond length is equal to the sum of L5 and L6 - Scheme 1). The L3 and L4 parameters are also characterized by low values of variance as one can observe for C−C bond length (the sum of L3 and L4 is equal to the C−C. bond length).

The meaningful values of variances are revealed for L1 and L2, which is not a surprising result. L1 is the radius (the distance between the X-attractor and BCP of C-X bond) of the X-atom substituent. Since the variety of X-substituents is taken into account thus the variance is relatively high, 0.051 for all subsamples. One can observe that these radii for the given substituent do not change for different subsamples. For example for the fluorine atom L1 amounts to 0.931, 0.928 and 0.940 Å for Y = H, F, and Li, respectively. If the subsample where Y = F is considered thus the mean L6 value amounts to 0.932 Å (the 0.925−0.940 Å range). This means that the atomic properties are often constant if one considers different classes of compounds and this is in line with one of the main concepts of the “atoms in molecules” theory (recently often named as

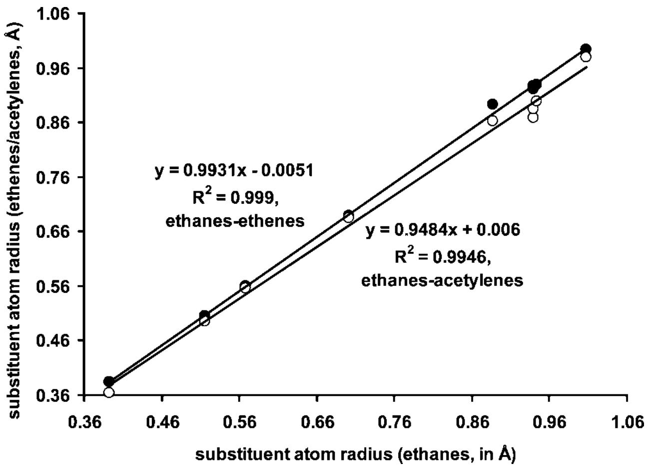


**Figure 1.** The relationship between the substituent atom radius (L1 according to the Scheme 1) of ethane derivative and the radius of ethene derivative (black circles) as well as the relationship between the radius of ethane derivative and the radius of acetylene derivative (open circles); the Y = Li subsamples are considered, all radii in Å.

QTAIM) that atoms in any species transfer their unique properties into the other species. For example, the transferability of atomic and group properties for hydrocarbons and silanes was analyzed.[33] It was found that the energy of the $A_nH_{2n+2}$ species (A = C or Si) may be expressed by the following equation: $E(A_nH_{2n+2}) = 2E(AH_3) + pE(AH_2)$, where p is the number of $AH_2$ groups within the moiety ($p = n - 2$). One can see that each $AH_2$ and $AH_3$ group is characterized by an amount of energy which is transferred from the one species to the other one. In the other study there is the analysis of the systems containing carbonyl group.[34] XCOY are considered and the properties of the C and O atoms in the carbonyl group are directly related to the nature and electronegativity of the X-substituent and to the character of Y group. It was found that the atomic energies of C and O atoms are less sensitive to the substituent effects than their volumes. Similarly, it was found[35] that the proton energies in the protonated $CH_3(CH_2)_nO(CH_2)_mCH_3$ molecules practically change slightly if considered for different species. One can see that the transferability of the energetic properties of atoms and/or groups is often observed while the other atomic properties are harder transferable.

For the species analyzed here the X-atom substituents radii are almost the same for the corresponding acetylene and ethane derivatives. Figure 1 presents the correlations between the X-substituent radii (L1-values). The X-radius of ethane derivative is related to the corresponding X-radius of ethene derivative and to the X-radius of acetylene one. This means that for the $X-CH_2-CH_2-Y$ molecule the corresponding $X-CH{=}CH-Y$ and $X-C{\equiv}C-Y$ species are taken into account. There are accurate linear correlations of the $y = ax + b$ type. The corresponding subsamples with Y = Li were analyzed (Figure 1). It is worth mentioning that the excellent correlations presented in Figure 1 are fulfilled for all pairs of subsamples (three subsamples of ethane derivatives considered here and the corresponding six subsamples of ethene and acetylene derivatives analyzed earlier). One can observe (Figure 1) that *a* and *b* coefficients are close to the unity and zero, respectively ($y \approx x$). This also supports the other findings that the substituents' properties are transferred between different classes of compounds.

Figure 1 also shows that for the correlation between ethane and ethene derivatives the *a*-coefficient is equal to 0.99 while for the correlation between ethane and acetylene derivatives it amounts to 0.95. This means that the slight systematic differences exist for the corresponding substituents' radii of acetylene, ethene and ethane derivatives; they increase respectively. This may mean that there is the slight electron charge transfer from C=C and C≡C bonds into C−X and C−Y single bonds. This causes their slight shortening. Thus one can see the interrelations between the CCY fragment and the X substituent. One can conclude that the substituent properties are roughly transferable however the slight systematic changes are observed if different −CCY fragments are considered, i.e.: −C−CY, −C=CY and −C≡CY.

For ethane derivatives where a $\sigma$ C−C bond exists, the radii are the greatest. One can observe that L1 value is the greatest for Na-substituent while it is the smallest for H-atom. However, the other values are not in agreement with the so-called atomic radii often presented and cited in various monographs.[36] The border H and Na L1 results presented here (Tables 1−3) are in agreement with the values of atomic covalent radii but this is not the rule for the other substituents. For example, the large L1 value of fluorine may be surprised since its atomic covalent radius is rather small. However, it is worth mentioning that the covalent atomic radii were determined from the geometries of homonuclear diatomic molecules. Thus for $F_2$ molecule the F-radius approximately amounts to 0.7 Å while for F−C bond considered here the BCP is shifted to the carbon attractor. Besides the atomic QTAIM radius is defined as the attractor−BCP distance and generally for the same atom is different for various types of bonds. This is in line with the recent studies on atomic properties of selected biomolecules. [37,38] The cluster analysis was performed to consider the properties of carbon atoms. Seven atomic properties were considered: kinetic energy, volume, population, and dipole, quadrupole, octupole and hexadecapole moments. The cluster analysis indicated two representations of carbon atoms: cruder one with 5 atom types and finer one with 21 atom types. Thus one can see that the atomic properties depend on the environment, in the other words these properties are transferable but only if the species considered are strongly related.

The relatively great variances of 0.13, 0.13 and 0.11 for the Y = H, F, and Li subsamples, respectively are observed for L2-values (Tables 1−3). There are also the similar, if not analogous, correlations and observations for L2 values as those presented for L1 values. This means that the substituents influence the C-X bonds as well as the corresponding L1 and L2 radii. Figure 2 presents the correlations between the carbon radii measured in the direction of X-substituent. These are various relationships between ethanes and ethenes as well as between ethanes and acetylenes. The Y = H subsamples were considered and similarly as for Figure 1 the *a* and *b* coefficients of the linear regressions are close to the unity and zero, respectively.

The results presented here show that the substituent effects are transferable from one type of species to another. Tables and figures presented show that the affected parameters (L1 and L2) correlate between themselves (Figures 1 and 2) not only for subsamples of ethane derivatives but this also holds for the other compounds (acetylene and ethane derivatives). Such correlations could not be found for commonly analyzed and compared energetic and geometrical parameters. Figure 3 shows the dependencies between C−C bond lengths for corresponding X-substituents. It indicates that the first subsample of ethane derivatives (Y = H) is related to the second subsample (Y = F) and to the third (Y = Li) one. There are no suitable correlations revealed. The similar lack of correlations is noticed

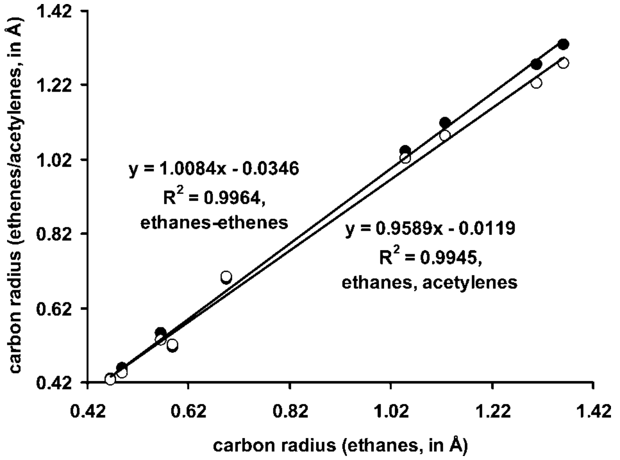


**Figure 2.** The relationship between the carbon atom radius (L2 according to the Scheme 1) of ethane derivative and the radius of ethene derivative (black circles) as well as the relationship between the radius of ethane derivative and the radius of acetylene derivative (open circles). The Y = H subsamples are considered, with all radii in Å.

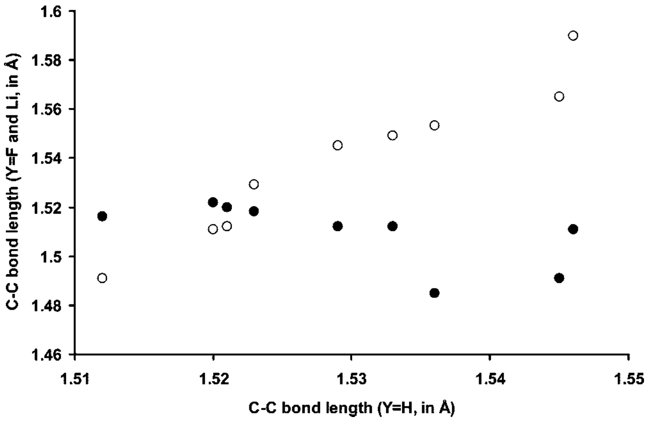


**Figure 3.** Relationship between C−C bond length (L3 + L4) for Y = H subsample and this bond length for Y = F (black circles) or Y = Li subsample (open circles), with bond lengths in Å.

if the related subsamples of unsaturated hydrocarbons are considered. The low variances for bond lengths may be the reason of such a situation. Hence one can see that bond lengths are not suitable parameters to detect and analyze substituent effects.

The sum of diameters of carbon atoms may be applied as a useful parameter to analyze substituents' effects. This is equal to L2 + L3 + L4 + L5. It was shown earlier that for acetylene and ethene derivatives such diameters correlate between themselves if the same substituents are considered. Figure 4 shows similar correlations where the subsamples presented in Tables 1−3 are considered. The Y = H subsample is related to Y = F and to Y = Li subsamples. One can see that the sum of diameters is the largest for Y = Li derivatives, less for Y = F ones, and the shortest for Y = H. It was found that such diameters correlate between themselves if acetylene and ethene derivatives are analyzed. There are no such correlations between ethane derivatives or any other subsamples of unsaturated hydrocarbons. This means that for ethane derivatives the substituents influence the BCPs' locations in different way than for such $\pi$-electron compounds as ethene and acetylene derivatives.

It was mentioned here before that bond lengths as well as L3 and L4 parameters are insensitive on the substituent effects since the low values of variances were predicted for them.

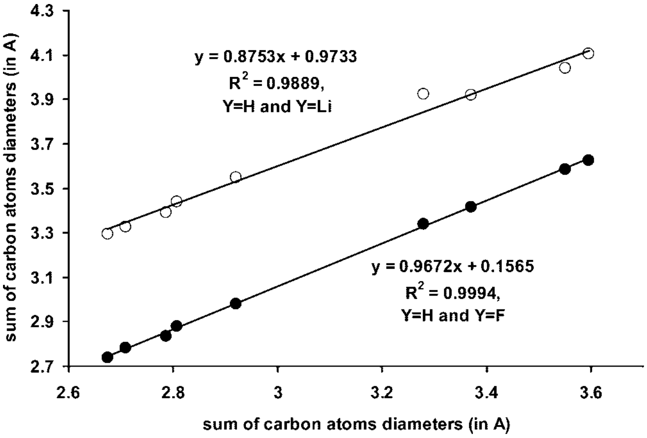


**Figure 4.** The correlation between the sum of the carbon atoms' diameters (L2 + L3 + L4 + L5) for Y = H subsample and this sum for Y = F (black circles) or Y = Li subsample (open circles), with the diameters' sum in Å.

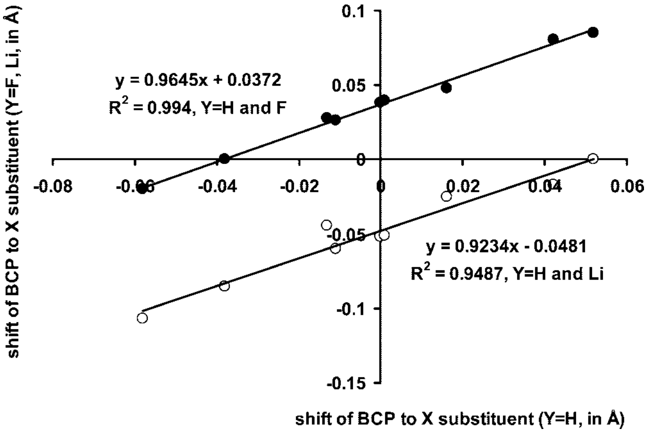


**Figure 5.** The correlation between the shift of C−C BCP from the midpoint to the X-substituent for *Y* = H subsample and this shift for Y = F (black circles) or Y = Li subsample (open circles), with the shifts in Å.

However the shift of BCP to the X-substituent may be considered (Figure 5) which in the extreme cases is of about 0.1 Å; for $NO_2-CH_2-CH_2-Li$, it is equal to −0.107 Å, while in the case of $Li-CH_2-CH_2-F$, it amounts to 0.085 Å. Hence, the shift range amounts to 0.192 Å. For comparison, the range for the C−C bond length is equal to 0.080 Å. There are the linear correlations between such shifts if different subsamples of ethane derivatives are considered. In the other words the BCP within C−C bond region moves from the midpoint and such a displacement depends on the type of substituents. It is worth mentioning that there is the much greater shift of BCP to the X-substituent in the case of ethylene and acetylene derivatives.[28,29] The shift range amounts to 0.352 and 0.562 Å for ethylenes and acetylenes, respectively. The range for C=C and C≡C bond lengths is equal to 0.052 and 0.075 Å, respectively. One can see that for all simple derivatives of acetylene, ethylene and ethane the changes in CC bond length are meaningless while in the case of the CC BCP position they are more important for $\pi$-electronic species than for single C−C bonds. This is since the double and triple bonds are easier polarizable and hence more reactive than the single bonds.[39]

## Summary

It was shown that for some types of the species considered in this study the traditional parameters may be insensitive on

the substituents' effects, or at least the systematic changes of these parameters are not revealed. The ethane derivatives were analyzed and it is obvious that such systematic changes do not involve C−C bond length, the electron density at the corresponding BCP and its laplacian. However, if positions of BCPs are taken into account thus numerous correlations may be observed. The L1 and L2 radii correlate between themselves for different subsamples of ethane, ethene and acetylene derivatives. The characteristics of substituent atoms are practically preserved in different compounds since their radii change only slightly.

The most interesting result relates to the location of BCP of C−C bond. It moves if different substituents are considered and these are systematical displacements from the midpoint of C−C bond. The considered here sum of carbon diameters for the subsample of ethane derivatives (where Y = H), increases following the sequence of X-substituents: F, OH, $NO_2$, $NH_2$, H, $BH_2$, BeH, Na, and Li. This sequence only slightly changes for the increase of diameters' sum for the subsamples with Y = F, Li. However, if the shift of C−C BCP for Y = H subsample is considered its range is from −0.058 to +0.052 Å. The shift of the BCP for this subsample changes according to the following sequence of X-substituents: $NO_2$, F, $NH_2$, OH, H, $BH_2$, BeH, Na, and Li. One can also observe the approximate changes of the latter parameters (shift and diameter) if electronegativity of substituent decreases.

One can see that there is only meaningless dependence (or it is even not observed) between the substituent and molecular properties if the traditional geometrical parameters are considered since there are not any correlations between them. The consideration of the BCP position shows that such interrelations exist. This is the novel and interesting finding that the substituent effects may be observed for $\sigma$ CC bond.

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