ORIGINAL RESEARCH

On differences in substituent effects in substituted ethene and acetylene derivatives and their boranyl analogs

Mirosław Jabłoński[1] · Tadeusz M. Krygowski[2]

Abstract

This article is the first attempt to present different influence of substituent effects on double and triple bonds and, conversely, to present the impact of these bonds on the electronic structure of substituents. For this purpose, quantum-mechanical calculations were made for X-substituted derivatives of ethene and acetylene with 27 diverse substituents representing a wide spectrum of electronic properties, from strongly electron-accepting to strongly electron-donating ones. In addition to these systems, their boranyl derivatives are also investigated. It turns out that the Hammett substituent constants do not correctly describe changes in the CC bond length in any of the considered family of systems. However, the relationships with the CB bond length are significantly better. It is shown that the triple bond in acetylene derivatives is much more resistant to external perturbations than the double bond in the analogs containing an ethene unit. As a consequence, in acetylene derivatives, the substituent effects on CC bond length are about half of the substituent effects in ethene derivatives. We suggest that the observed lack of a clear linear correlation between the length of the CC triple bond in acetylene derivatives and the value of electron density on this bond is due to the disturbing additional interaction between the structure of the X substituent in the xy plane and the π bond being in the same plane in the acetylene unit—on the contrary, this interaction is not possible in ethene analogs.

Keywords Acetylene · Boranyl · Ethene · Substituent · Substituent effect

Introduction

Quantitative approaches to the problems of substituent effects (SE) in organic chemistry originate from the fundamental works by L. P. Hammett [1, 2] by introduction of substituent constants:

$$\sigma_{p/m} = \lg \frac{K_X}{K} \tag{1}$$

✉ Mirosław Jabłoński
teojab@chem.umk.pl

1 Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100, Toruń, Poland

2 Department of Chemistry, Warsaw University, Pasteura 1, 02-093, Warsaw, Poland

where K_X and K are dissociation constants for *para/meta*-X-substituted and unsubstituted benzoic acids, respectively, and the acid-base reaction reads as follows:

$$XPhCOOH + H_2O \overset{K_X}{\rightleftarrows} XPhCOO^- + H_3O^+ \tag{2}$$

The relationship between the influence of substituents X on the physicochemical properties P (e.g., kinetic constants, equilibrium constants, spectral or electrochemical properties for benzene derivatives) and $\sigma_{p/m}$ constants is described by the Hammett equation:

$$P(X) = \rho\sigma_{p/m} \tag{3}$$

where ρ is the so-called reaction constant that describes the sensitivity of the reaction under study (physicochemical process) to the effect of X. Hammett substituent constants represent the numerical characteristics of electron accepting/donating properties of substituents and have become a very convenient way for describing most of substituent effects encountered in physical organic chemistry. Then, an avalanche of papers has appeared that have undertaken these problems presented and summarized in a numerous reviews and monographs [3–11].

In most cases, the substituted systems were either benzene or some aromatic system derivatives, and much less frequently unsaturated systems or those with triple bonds. Moreover, usually the problem considered was rather the substituent effect on some physicochemical properties of the systems with a particular group fixed in the series like X–R–Y and rather rarely concentrated on the changes of electronic structure of the substituents which have participated in this kind of interactions. To some extent, it was due to the method of interpretation of the SE by use of the Hammett substituent constants σ_m, σ_p which could take into account usually these aspects and in most cases in standard situations as in benzoic acids or alike [12]. In other cases, differently defined substituent constants like σ^+, σ^-, R, I, etc., were in use [11].

Applications of the quantum chemistry methods [13] for describing SE have changed the situation substantially. An atomic charge computed for a given substituent, $q(X)$, allows showing how its electronic structure changes in dependence on the molecule to which it is attached as well as on the position of the attachment. In some cases, a useful way is to apply charge of the substituent active region, abbreviated as cSAR(X), equal to the sum of atomic charges of all atoms of the substituent X and the substituted carbon atom C_{ipso} [14–16]:

$$cSAR(X) = q(X) + q(C_{ipso}) \qquad (4)$$

This way of presentation of electronic structure of the substituent has substantially opened possibilities to learn about changeability of the substituent electronic properties in dependence on the environment of its attachment. Undoubtedly, cSAR(X) values depend on the kind of carbon atom to which the substituent is attached and comparisons are allowed only if these atoms are strongly alike. It may be assumed that cSAR(X) for substituted benzene and e.g. butadiene may be still allowed to be compared, but this kind of comparison for acetylene and ethene derivatives seems to be not acceptable.

Unlike the earlier mentioned systems, acetylene derivatives have not been subject of too many systematic studies with substituent effects as a main topic. Some more important papers have to be mentioned. Most likely the first ab initio studies on substituted acetylene derivatives were performed by Powell et al. [17] in 1983 and concerned the description of the influence of substituent effects on the acidity of an acetylene hydrogen atom. Then, substituent effects on acetylene stability were studied using isodesmic methyl exchange reactions [18]. Detailed NMR studies of substituted acetylene derivatives were performed by Kamienska-Trela et al. [19] and Wiberg et al. [20]. The heats of formation of some haloacetylenes [21, 22] and polyacetylenes [23] were also computed. The substituent

effects in acetylenes and ethylenes were also studied [24] by Quantum Theory of Atoms in Molecules (QTAIM) [25]. Quite recently, we have performed a comparative analysis of the electronic structure in substituted acetylene and diacetylene derivatives [26]. Various spectroscopic parameters for the latter group of compounds were calculated by Roman et al. [27]. Most of the important information on chemistry of acetylene and its derivatives are gathered in monograph by Diederich, Stang, and Tykwinski [28].

As already mentioned, Hammett substituent constants and their further modifications were introduced for *para/meta*-X-substituted benzoic acid [1, 2] and for this reason they were used to describe the substituent effects only in more or less complex benzene derivatives, while there are no studies on the applicability of these constants in non-aromatic systems, but containing double or triple bonds or some conjugated variants thereof. The simplest representatives of compounds containing such bonds are, respectively, ethylene and acetylene. Comparing the π-electron structure in both of these molecules, it can be expected that the electronic effects related to the presence of the X substituent should be different in them, which results from the fact that in ethylene the double bond occurs only in one plane, while in acetylene both π bonds are in two planes perpendicular to each other. This difference in the π-electron structure should manifest itself in some way during the interaction with the substituent X. It should be emphasized here that the simple theoretical parameter cSAR(X) [14–16], used to describe the substituent effects, cannot be utilized in this case due to the fact that the carbon atoms are too different in both these molecules. Therefore, we have undertaken, what is the main purpose of this article, to perform a comparative analysis between substituent effects on ethene and acetylene derivatives. To some degree, this is continuation and substantial extension of the studies presented in our former article [26] in which there were presented substituent effects on acetylene and diacetylene derivatives themselves.

In addition to X-substituted ethylene and acetylene, we also investigate substituent effects on their boranyl derivatives. The boranyl group, as having an empty $2p_z$ orbital, has very specific electronic properties [29–31], as it can act as a strong electron charge acceptor. At the same time, the flatness of this group enables easy coupling with the adjacent π-electron system, creating good conditions for charge relocation. The situation is thus somewhat similar to that which characterizes the amino group: although the population of the $2p_z$ orbital in both groups is opposite, there is as an electron pair vacancy in the former, whereas the lone electron pair in the latter. Thus, in terms of electronic properties, both of these groups, i.e., -NH$_2$ and -BH$_2$, are opposite ends of the same stick. This makes studies on the effect of the type of CC bond on the interaction of the -BH$_2$ group with various substituents particularly interesting.

In the studies presented here, 27 X substituents with the full spectrum of electronic properties are used, from strongly electron-withdrawing to strongly electron donating, as described by the Hammett σ_p constant. As for historical reasons [1, 2], the substituent constants are commonly used only to describe substituent effects on various benzene derivatives [3–12], one of the main and most interesting aims of this research is to investigate the applicability of the substituent constant σ_p in describing substituent effects in X-substituted ethene and acetylene derivatives. This is the first study of this issue. It is worth recalling at this point that the use of cSAR(X) [14–16] seems to be unacceptable here because of too much different *ipso*-carbons in both types of compounds investigated. As part of the presented research, the following issues will be discussed:

1. How much the X··· Y (Y = H, BH$_2$) interaction changes delocalization in double-bonded systems in comparison with the triple-bonded ones
2. How double-bonded moieties change electron structure of substituents and the -BH$_2$ group in comparison with the triple-bonded moieties
3. A difference in ability of charge transfer via double and triple bond(s)

Methodology

All calculations were performed at the ωB97X-D/6-311++G(2df,2p) level of theory, that is utilizing the ωB97X-D exchange-correlation functional [32, 33] of Density Functional Theory (DFT) [34–36] and the 6-311++G(2df,2p) basis set [37–41], including both polarization and diffuse functions.

At the beginning, the geometries of X-substituted (X ∈{-NO$_2$, -CN, -CHO, -CFO, -CClO, -CMeO, -CONH$_2$, -COOH, -COOMe, -CF$_3$, -OCN, -NCO, -SCN, -NCS, -BH$_2$, -CCH, -CCF, -H, -F, -Cl, -Me, -OH, -SH, -OMe, -NH$_2$, -NHMe, -NMe$_2$}, where Me = CH$_3$) ethene, acetylene, and their respective boranyl derivatives (i.e., having Y = BH$_2$) were fully optimized. To increase the accuracy of the optimization procedure and numerical integration, cutoffs on forces and step size that are used to determine convergence were additionally tightened (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) and integration grid was increased to the (99, 590) one (UltraFine) having 99 radial shells and 590 angular points per shell. The fact of being true minima on the potential energy hypersurface has been confirmed by the lack of imaginary frequencies in vibrational analysis. These calculations were performed by means of the Gaussian 09 program [42]. In the case of

X-substituted boranylethene derivatives, the more extended *trans* conformation was used. For simplicity, the -C=C- and -C≡C- transmitting units in XRY molecules will be labeled as En and Ac, respectively. Fully optimized structures of boranyl derivatives are shown in Figs. 1 (XEnBH$_2$) and 2 (XAcBH$_2$) for reader's convenience. Of course, they are derivatives of their counterparts in which instead of the -BH$_2$ group there is a hydrogen atom, i.e., Y = H. The latter are therefore easy to imagine.

The values of electron density at critical points [25] of CC bonds were computed using the AIMAll program [43]. Electron densities at bond critical points are often used [25] as descriptors of the strength of various chemical bonds and intermolecular interactions.

Atomic charges were computed utilizing Multiwfn [44] program and the Voronoi Deformation Density (VDD) method [45–47]. Earlier it was shown that VDD atomic charges are highly reliable [31, 47, 48] and, importantly, almost independent of the computational method used to determine them [47]. The charge difference $\Delta q_{XH} = q(H) - q(X)$, i.e., determined for the terminal hydrogen atom and group X, was used in the analysis of charge distribution in the examined systems. This parameter should be identified with the polarization of the XRY molecule rather than with the X→Y charge transfer effect, which was instead determined using the most recently introduced definition [26]:

$$CT_{X \to Y} = \min\{\Delta q_X, |\Delta q_Y|\} \qquad (5)$$

where

$$\Delta q_X = q_X(XY) - q_X(XX) > 0 \qquad (6)$$

$$\Delta q_Y = q_Y(XY) - q_Y(YY) < 0. \qquad (7)$$

In Eq. 6, $q_X(XY)$ and $q_X(XX)$ denote the charge of the X substituent in the XRY and XRX systems, respectively. The same applies to the charge of group Y in Eq. 7. Importantly, the definition given by Eq. 5 takes into account the following facts: (i) group Y cannot accept more charge from X than this group donates (ii) both groups, i.e., X and Y, already had some charge before the charge transfer occurs (iii) the "own group charges" can be determined from the symmetrical XRX and YRY systems, in which the charge transfer effect is not possible [26].

Results and discussion

When CC bond lengths (d_{CC}) in X-substituted acetylene (XAcH) and X-substituted acetyleneborane (XAcBH$_2$) derivatives are compared (see Table 1), it results in the range of observed CC bond lengths being somewhat greater for
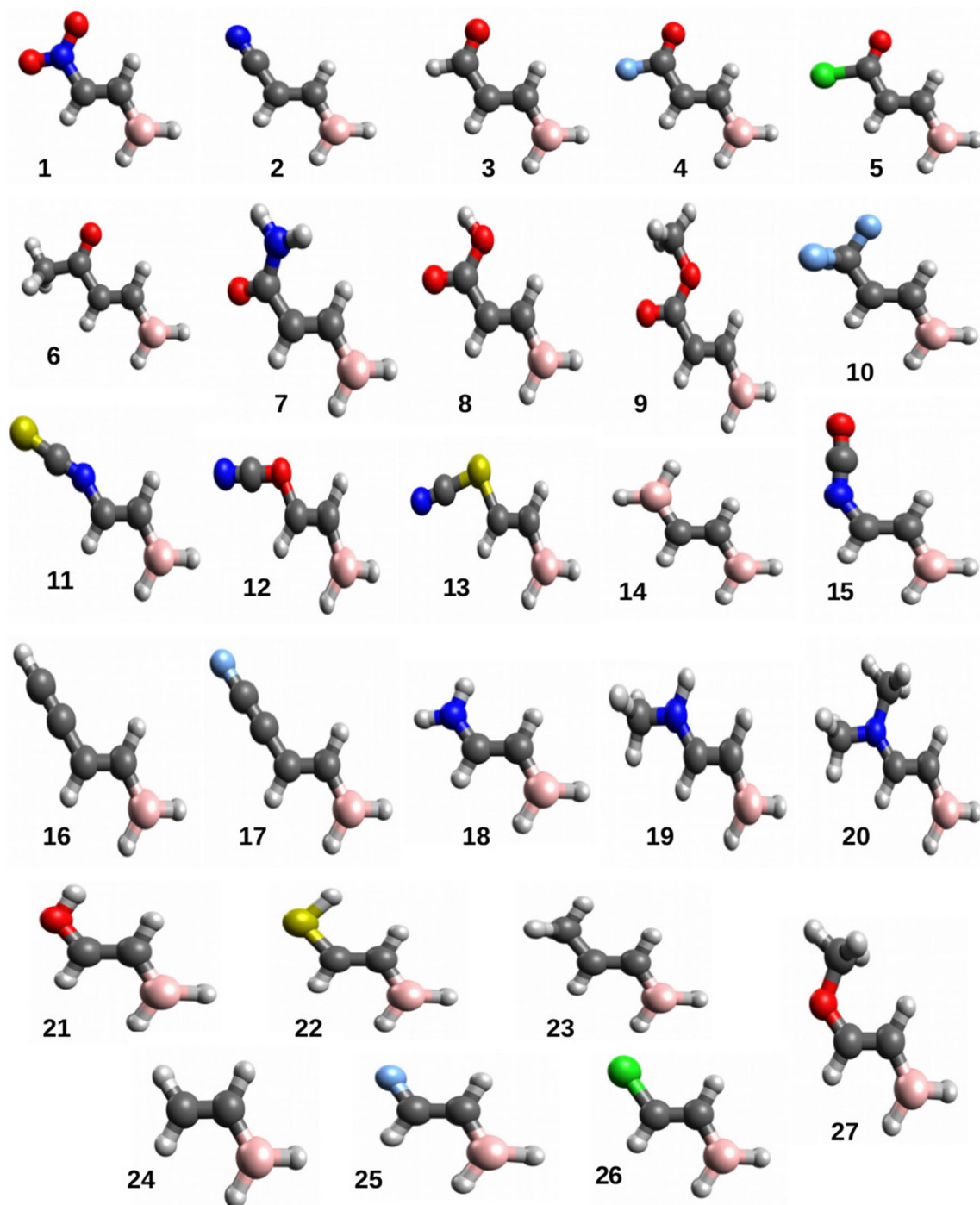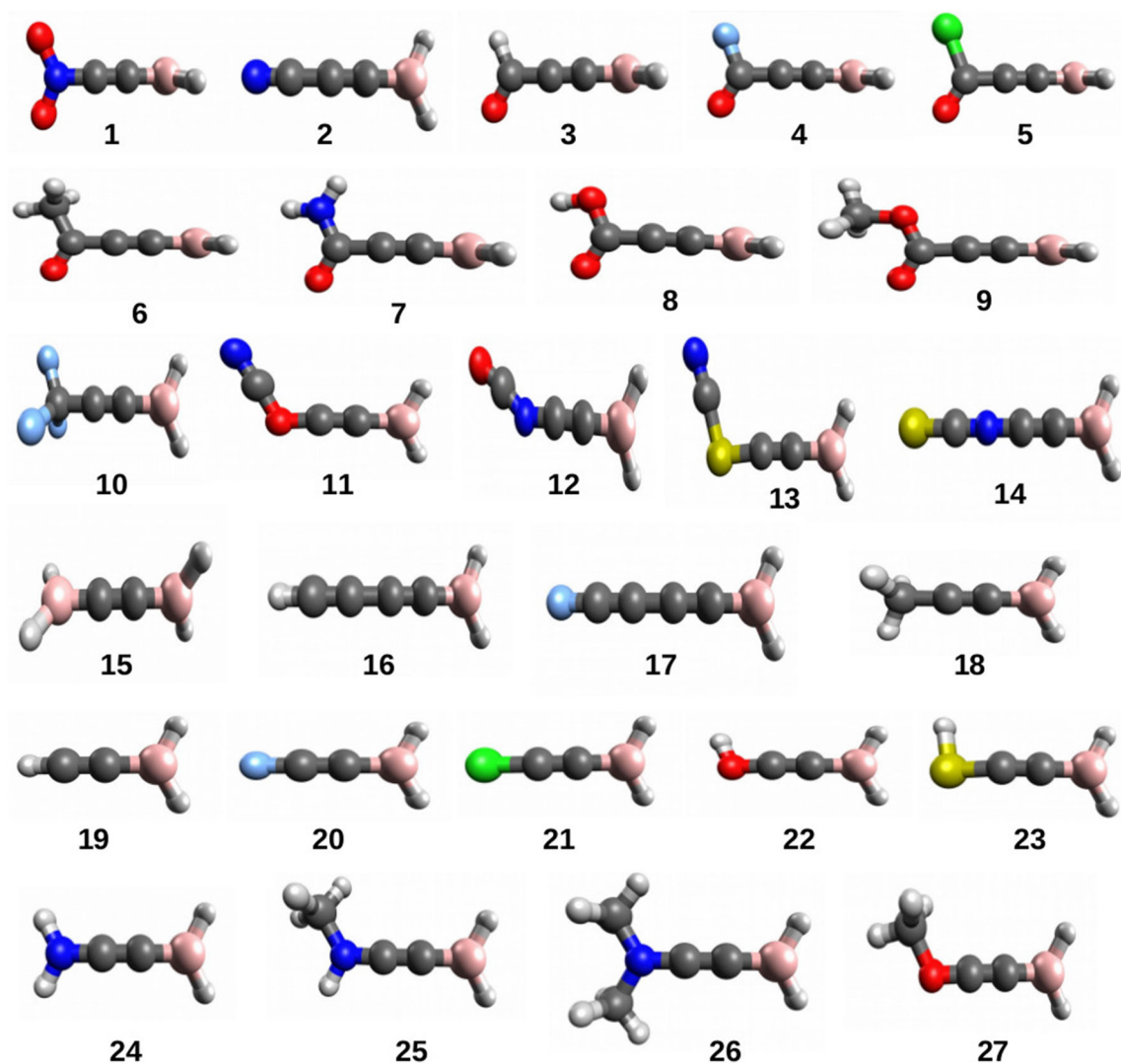
Fig. 1 Fully optimized structures of XEnBH$_2$ (X = -NO$_2$ (1), -CN (2), -CHO (3), -CFO (4), -CClO (5), -CMeO (6), -CONH$_2$ (7), -COOH (8), -COOMe (9), -CF$_3$ (10), -NCS (11), -OCN (12), -SCN (13), -BH$_2$ (14), -NCO (15), -CCH (16), -CCF (17), -NH$_2$ (18), -NHMe (19), -NMe$_2$ (20), -OH (21), -SH (22), -Me (23), -H (24), -F (25), -Cl (26), -OMe (27)

the latter (0.023 Å) than for the former (0.017 Å), giving an increase by 0.006 Å. Comparisons made for the X-substituted etheneboranes and ethenes result in 0.043 Å and 0.024 Å, respectively, giving an increase by 0.019 Å.

Thus, the effects of substituent on CC bond lengths are significantly smaller for substituted acetylene than ethene derivatives and in both cases the boranyl functional group increases clearly the observed effects, in particular in the case of ethenes. This may indicate a greater resistance of the triple CC bonds than of the double ones for external perturbations and most likely results from much higher force constants of the former compared to the latter.

Fig. 2 Fully optimized structures of $XAcBH_2$ (X = $-NO_2$ (1), $-CN$ (2), $-CHO$ (3), $-CFO$ (4), $-CClO$ (5), $-CMeO$ (6), $-CONH_2$ (7), $-COOH$ (8), $-COOMe$ (9), $-CF_3$ (10), $-OCN$ (11), $-NCO$ (12), $-SCN$ (13), $-NCS$ (14), $-BH_2$ (15), $-CCH$ (16), $-CCF$ (17), $-Me$ (18), $-H$ (19), $-F$ (20), $-Cl$ (21), $-OH$ (22), $-SH$ (23), $-NH_2$ (24), $-NHMe$ (25), $-NMe_2$ (26), $-OMe$ (27)

It is important to indicate that any relationships are not observed between the CC bond lengths and the characteristics of substituents described by the substituent constants σ_p, F, and R (see Fig. S1). For example, the linear regressions of d_{CC} on σ_p lead to determination coefficients $R^2 < 0.35$ for acetylenes and ethenes and significantly better for their boranyl derivatives, but still not sufficient to be subject of any deeper analyses. It may be concluded that the substituent constants while very effective in interpretation of manifold physicochemical properties of X-R-Y fail in the case of describing the substituent effects on CC bond lengths of substituted ethene and acetylene derivatives.

Situation is clearly better for dependence of CB bond lengths (d_{CB}) on the σ_p, R (Fig. 3) and F (Fig. S2) substituent constants.

In the case of σ_p, the determination coefficients for $XEnBH_2$ and $XAcBH_2$ are 0.805 and 0.745, respectively. Interestingly, for substituents with $\sigma_p < 0$ (i.e., electron-donating) both linear regressions are clearly better since determination coefficients improve to 0.861 and 0.937, respectively (see the light blue and black fitting lines in the upper subfigure of Fig. 3). However, this may result from a smaller variety of electron-donating substituents in our set of X. For the constant R, the values of the determination coefficients are somewhat better than those for σ_p and amount to 0.885 and 0.780 for $XEnBH_2$ and $XAcBH_2$, respectively. This result suggests that the interaction between the X substituent and the CB bond is mainly resonance in nature.

Interesting dependence is observed when CC bond lengths in XAcH and $XAcBH_2$ are plotted against these

Table 1 Values (in Å) of CC bond lengths in XAcH, XAcBH$_2$, XEnH, and XEnBH$_2$

| X	σ_p[a]	XAcH	XAcBH$_2$	Δ	XEnH	XEnBH$_2$	Δ
BH$_2$	–	1.205	1.223	0.018	1.337	1.349	0.012
NO$_2$	0.78	1.191	1.205	0.014	1.316	1.325	0.009
CFO	0.70	1.195	1.208	0.014	1.325	1.336	0.011
CN	0.66	1.196	1.208	0.012	1.327	1.340	0.013
CClO	0.61	1.196	1.210	0.014	1.326	1.336	0.011
CF$_3$	0.54	1.192	1.203	0.011	1.319	1.331	0.013
OCN	0.54	1.188	1.203	0.014	1.313	1.328	0.015
SCN	0.52	1.197	1.214	0.017	1.321	1.338	0.017
CMeO	0.50	1.197	1.211	0.014	1.325	1.337	0.012
COOH	0.45	1.195	1.208	0.013	1.325	1.337	0.012
COOMe	0.45	1.195	1.208	0.013	1.324	1.337	0.013
CHO	0.42	1.198	1.211	0.014	1.327	1.338	0.012
NCS	0.38	1.198	1.213	0.015	1.325	1.342	0.017
CONH$_2$	0.36	1.196	1.209	0.013	1.325	1.339	0.014
Cl	0.23	1.194	1.207	0.013	1.317	1.333	0.016
AcH	0.23	1.199	1.213	0.013	1.329	1.346	0.017
NCO	0.19	1.196	1.209	0.014	1.325	1.344	0.019
SH	0.15	1.199	1.216	0.018	1.324	1.345	0.021
F	0.06	1.189	1.202	0.013	1.315	1.331	0.016
AcF	–	1.199	1.212	0.013	1.329	1.346	0.017
H	0.00	1.194	1.205	0.011	1.322	1.337	0.015
Me	−0.17	1.197	1.209	0.012	1.324	1.342	0.018
OMe	−0.27	1.196	1.213	0.016	1.329	1.350	0.022
OH	−0.37	1.194	1.210	0.016	1.325	1.346	0.022
NH$_2$	−0.66	1.198	1.220	0.022	1.330	1.359	0.029
NMeHy	−0.70	1.200	1.223	0.023	1.332	1.364	0.031
NMe$_2$	−0.83	1.201	1.225	0.024	1.336	1.368	0.032
Average	–	1.196	1.211	0.015	1.325	1.342	0.017
Range	–	0.017	0.023	0.006	0.024	0.043	0.019

[a]All X substituents except -BH$_2$ and AcF are ordered in descending order of σ_p values [9], i.e., from most electron-withdrawing to most electron-donating

bond lengths for their ethene-based analogs, i.e., XEnH and XEnBH$_2$, as presented in Fig. 4. The appropriate linear regressions are as follows: $d_{CC}^{XAcH} = 0.569\ d_{CC}^{XEnH} + 0.442$ with $R^2 = 0.815$ and $d_{CC}^{XAcBH_2} = 0.542\ d_{CC}^{XEnBH_2} + 0.484$ with $R^2 = 0.792$. In spite of the somewhat poor quality of linear regression, it may be concluded that in acetylene derivatives the substituent effect on the CC bond length is ca. 0.5 of that observed in ethene derivatives, and the boranyl group slightly decreases the substituent effects.

Very interestingly, the linear regressions between the CC bond distances, d_{CC}, and the electron density computed at the critical points [25] of these bonds (ρ_{CC}) have been found (in Fig. 5) to feature somewhat unexpected characteristics. Namely, the regression lines are well acceptable with $R^2 \geq 0.916$ for XEnH and XEnBH$_2$, i.e., the X-substituted ethene and etheneborane derivatives, whereas

for both the X-substituted acetylenes and the X-substituted acetyleneboranes a lack of any correlation is observed since $R^2 \leq 0.118$. The interpretation may be as follows. Assuming the C-X direction as the x axis (see Fig. 6), two kinds of interactions should be taken into account: (i) a direct interaction of electronic structure of the X substituent with its one π-electron bond in acetylene in xz plane, and (ii) an interaction of the planar structure of the substituent in xy plane with another π-electron bond in the acetylene unit. The latter interaction is most probably the reason of perturbation that causes lack of the simple relationship observed for acetylene derivatives. In contrast, such a perturbation is not possible in ethene derivatives, where the π-electron interaction can take place only in one plane. Obviously, the detailed characteristics of the interaction between the p_y orbital of the acetylene unit

Fig. 3 Relationships between d_{CB} and either σ_p or R
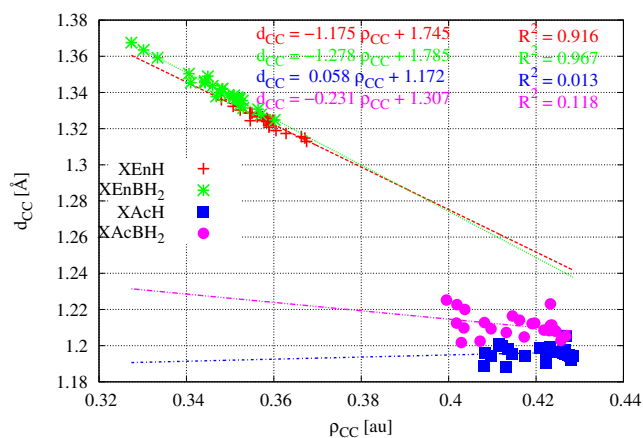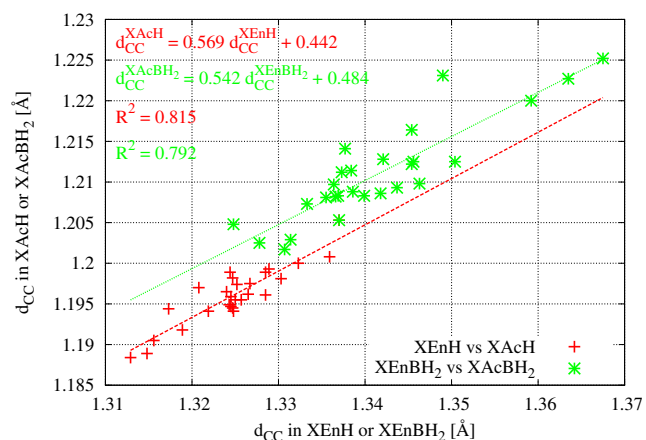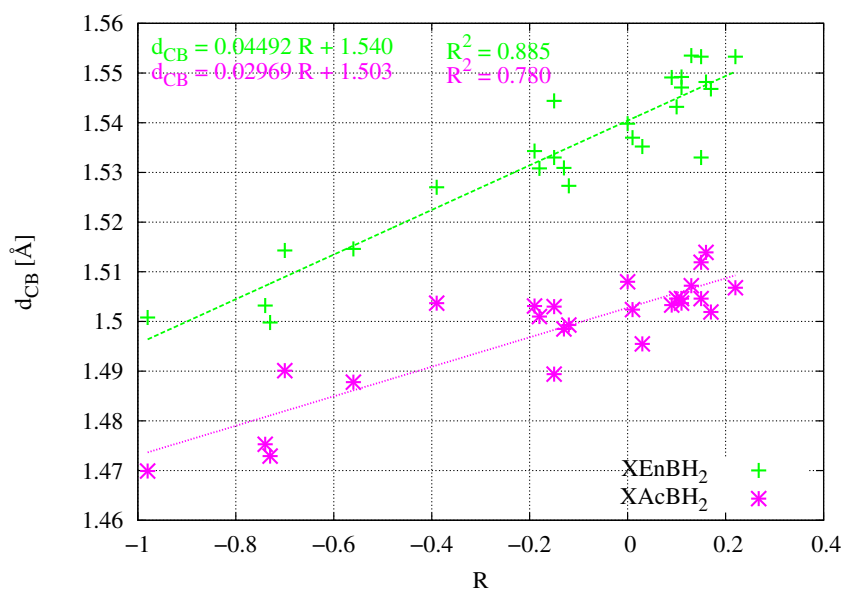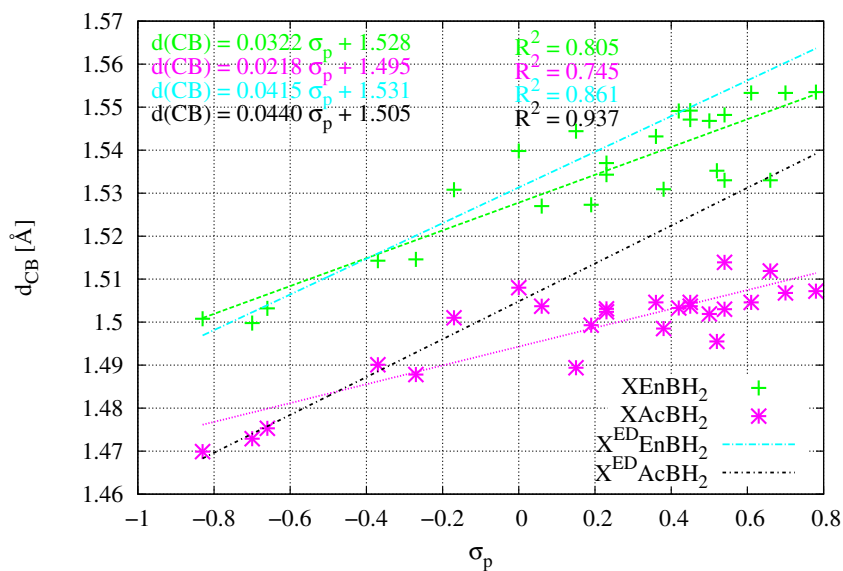
Fig. 4 Relationships between d_{CC}

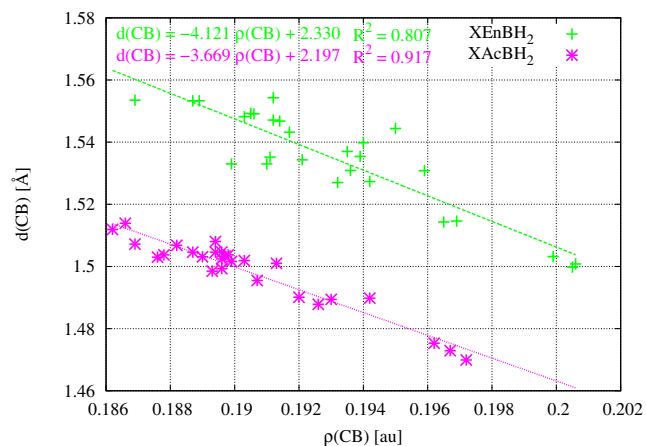**Fig. 5** Relationships between ρ_{CC} and d_{CC}
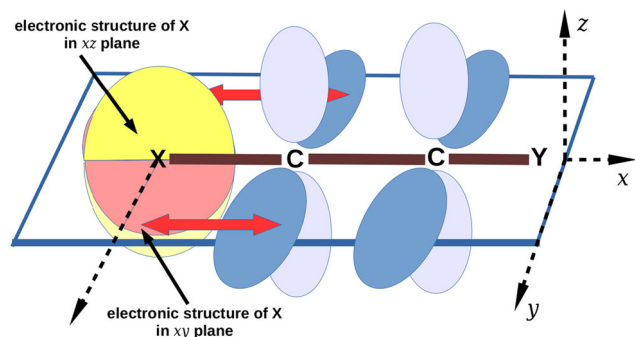
Fig. 6 Illustration of the interaction between the electronic structure of the X substituent and the p-orbitals of the acetylene unit in XAcY. The red arrows refer to point (ii) in the text

and the planar electronic structure of the substituent in the xy plane depend on the type (type, number, and spatial arrangement of atoms) of the substituent.

Of course, dispersion of points relative to the vertical axis d_{CC} visible in Fig. 5 confirms the previously discussed largest range of d_{CC} values obtained for XEnBH$_2$ (see also Table 1). It is also seen that the values of electron density determined at the critical point of the CC double bond in the analyzed ethenes are from 0.327 to 0.368 au and are significantly lower than the corresponding values for the CC triple bond in the acetylene derivatives in question (0.400–0.429 au). As a consequence, this significant difference makes the triple bond much stronger (having a greater force constant) and therefore less susceptible to external perturbations, such as substituent effects resulting from the presence of group X.

It is also worth mentioning about good, though slightly worse than for d_{CC} vs ρ_{CC} for the investigated ethene derivatives (Fig. 5), correlations between the length of the CB bond (d_{CB}) and the value of electron density at the critical point of this bond (ρ_{CB}). Values of R^2 amount to 0.807 and 0.917 for XEnBH$_2$ and XAcBH$_2$, respectively (see Fig. 7).

The somewhat smaller slope (-3.669) for the latter family of systems shows a slightly weaker relationship between ρ_{CB} and d_{CB}, i.e., the length of CB bond, which is most likely due to the disturbing axial charge relocation in the acetylene unit compared to the single-plane delocation in the ethene unit.

When charges of the substituents $q(X)$ are plotted against σ_p, F and R substituent constants [9], the situation is better than that observed for the CC bond length (see Fig. 8).
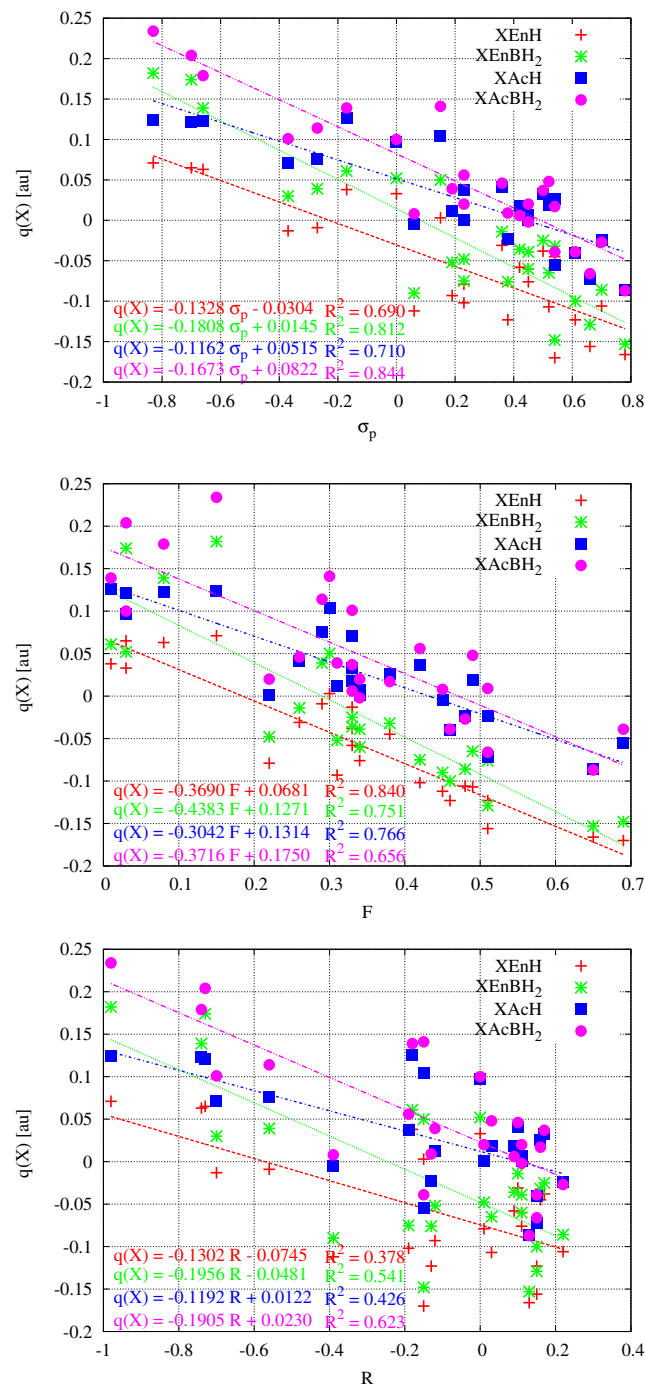
Fig. 8 Relationships between $q(X)$ and σ_p, F and R

Fig. 7 Relationships between ρ_{CB} and d_{CB}

In the case of substituent constants σ_p and R, these correlations are also better in the case of acetylene derivatives than in the case of ethene derivatives. However, the situation is reversed when the F substituent constant in considered instead. Interestingly, the presented data clearly show that for X-substituted ethene and acetylene derivatives, R^2 values are the largest for the substituent constant F (0.840 and 0.766, respectively). On the contrary, for their boranyl counterparts, R^2 values are the largest for the substituent constant σ_p (0.812 and 0.844, respectively). This result suggests that the electronic properties of the X substituent described by its charge, i.e., $q(X)$, are best suited to the inductive effect of this substituent, but the presence of the boranyl group increases the proportion of resonance interactions.

It was particularly interesting to study the effect of changing the double bond in the X-substituted ethenes on the triple bond in the X-substituted acetylenes on the electronic state of both the X substituent and terminal hydrogen atom. These states can be sampled using the charges $q(X)$ and $q(H)$ as well as their changes upon the step XEnH→XAcH. The corresponding values are listed in Table 2.

It is easy to see that the XEnH→XAcH step, i.e., the replacement of the double bond in XEnH by the triple bond in XAcH, increases the charge of the substituent X on the absolute scale (i.e., $\Delta q(X) > 0$). The same effect is also visible for the terminal hydrogen atom ($\Delta q(H) > 0$). Thus, compared to the double bond in the ethylene unit, the triple bond in the acetylene unit additionally pulls the electron charge from *both* the X substituent and the hydrogen atom. It is worth noting that, as a consequence, the hydrogen atom in substituted acetylenes is more acidic than in substituted ethenes.

**Table 2** Charges (in au) of X and H in XEnH and XAcH molecules and their changes upon the XEnH→XAcH step

X	σ_p^a	XEnH		XAcH		XEnH→XAcH	
		$q(X)$	$q(H)$	$q(X)$	$q(H)$	$\Delta q(X)$	$\Delta q(H)$
BH_2	–	0.000	0.042	0.089	0.100	0.089	0.058
NO_2	0.78	−0.166	0.075	−0.086	0.131	0.080	0.056
CFO	0.70	−0.106	0.063	−0.024	0.123	0.082	0.060
CN	0.66	−0.156	0.060	−0.072	0.124	0.084	0.064
CClO	0.61	−0.123	0.066	−0.040	0.123	0.083	0.057
CF_3	0.54	−0.045	0.058	0.026	0.119	0.071	0.061
OCN	0.54	−0.170	0.061	−0.055	0.112	0.115	0.051
SCN	0.52	−0.107	0.058	0.019	0.111	0.126	0.053
CMeO	0.50	−0.038	0.048	0.033	0.107	0.071	0.058
COOH	0.45	−0.076	0.054	0.001	0.114	0.077	0.060
COOMe	0.45	−0.060	0.050	0.007	0.110	0.067	0.060
CHO	0.42	−0.058	0.054	0.018	0.111	0.076	0.057
NCS	0.38	−0.123	0.048	−0.023	0.098	0.100	0.050
$CONH_2$	0.36	−0.031	0.049	0.041	0.105	0.072	0.056
Cl	0.23	−0.102	0.048	0.037	0.097	0.139	0.049
Ac	0.23	−0.079	0.044	0.001	0.101	0.080	0.057
NCO	0.19	−0.093	0.043	0.012	0.093	0.105	0.050
SH	0.15	0.003	0.034	0.104	0.091	0.101	0.057
F	0.06	−0.112	0.047	−0.005	0.096	0.107	0.049
AcF	–	−0.069	0.042	0.019	0.098	0.088	0.056
H	0.00	0.033	0.033	0.097	0.097	0.064	0.064
Me	−0.17	0.038	0.025	0.126	0.079	0.088	0.054
OMe	−0.27	−0.009	0.023	0.076	0.074	0.085	0.050
OH	−0.37	−0.013	0.027	0.071	0.079	0.084	0.051
NH_2	−0.66	0.063	0.011	0.123	0.070	0.060	0.059
NMeH	−0.70	0.065	0.008	0.121	0.066	0.056	0.057
NMe_2	−0.83	0.071	0.008	0.124	0.065	0.053	0.057

[a] All X substituents except -BH_2 and AcF are ordered in descending order of σ_p values [9], i.e., from most electron-withdrawing to most electron-donating

Like the relationships between d_{CC} values (Fig. 4), where data for X-substituted acetylene and acetyleneborane are plotted against the appropriate data for the ethene derivatives, the relationships between $q(X)$ values are also characterized by large R^2 values (see Fig. 9).

Moreover, they are clearly larger ($R^2 \geq 0.925$) than for d_{CC}. The appropriate linear regression equations are as follows: $q(X)^{XAcH} = 0.8352 \, q(X)^{XEnH} + 0.0764$ and $q(X)^{XAcBH_2} = 0.8749 \, q(X)^{XEnBH_2} + 0.0680$. In both cases, the slopes are less than 1.0, indicating that the acetylene moiety affects the charge of the substituent X weaker than the ethene moiety does. Moreover, since the slope for boranyl derivatives is slightly larger (0.875) than for the other systems (0.835), it may suggest that the boranyl functional group stimulates this increasing effect via resonance through the triple bond stronger than via a double bond.

The conductivity through a given system of bonds can also be studied by analyzing the value of the transferred charge from X to Y in the XRY system. This quantity is usually known as the charge transfer. Starting from the fact that the acceptor group Y cannot accept from donor X more charge than it donates, we have very recently proposed [26] calculating the value of the charge transfer by means of Eq. 5. Using this expression, it was interesting to compare the values of the transferred charge through double and triple bonds. This analysis was performed on the H_2NRNO_2 (R = En, Ac) systems containing a strongly electron-donating amino group on one end and a strongly electron-accepting nitro group on the other. The appropriate values of X and H charges as well as the transferred charge from the NH_2 group to the NO_2 group are shown in Table 3. The obtained results suggest that the charge transferred via the triple bond in H_2NAcNO_2 (0.122 au) is ca. 7% smaller than the charge transferred via the double bond in H_2NEnNO_2 (0.131 au).
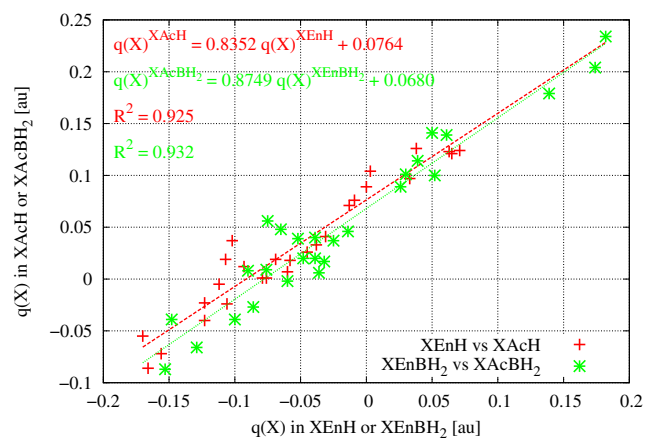
Table 3 Values of charge transfer (CT) computed (see Eqs. 5–7) for H_2NRNO_2 (R = En, Ac)

Molecule	$q(H)$	$q(NH_2)$	$q(NO_2)$	CT
HEnH	0.033	–	–	–
HEnNH$_2$	0.011	0.063	–	–
HEnNO$_2$	0.075	–	−0.166	–
H$_2$NEnNO$_2$	–	0.161	−0.245	0.131
H$_2$NEnNH$_2$	–	0.022	–	–
O$_2$NEnNO$_2$	–	–	−0.114	–
HAcH	0.097	–	–	–
HAcNH$_2$	0.070	0.123	–	–
HAcNO$_2$	0.131	–	−0.086	–
H$_2$NAcNO$_2$	–	0.203	−0.165	0.122
H$_2$NAcNH$_2$	–	0.001	–	–
O$_2$NAcNO$_2$	–	–	−0.043	–

Conclusions

The Hammett substituent constants do not describe properly substituent effects on CC bond length, neither in ethene nor in acetylene, nor in their boranyl derivatives. Relatively better are these relationships for CB bond lengths. We have found a much greater resistance against external perturbation in the case of CC triple bonds than in the case of CC double ones, so that in acetylene derivatives the substituent effect on bond length is approximately half of that observed in ethene derivatives. The substituent effects are then somewhat weakened when the BH_2 boranyl group is at the opposite end of the molecule to the X substituent.

In the case of both the ethene and etheneborane derivatives, the relationships between the CC bond distances, d_{CC}, and the charge density at the critical point of these bonds, ρ_{CC}, are well described by linear equations, whereas for their acetylene-based analogs lack of these dependences is observed, and is most probably due to an interaction of the planar structure of the substituent in xy plane with another π-electron bond in acetylene.

Compared to the double bond in the ethylene unit, the triple bond of the acetylene unit additionally draws an electron charge from both the X substituent and the terminal hydrogen atom, making this atom more acidic. The $NH_2 \rightarrow NO_2$ charge transfer via the triple bond in $H_2N-C\equiv C-NO_2$ is ca. 7% smaller than the amount of charge transferred via the double bond in $H_2N-CH=CH-NO_2$.

Fig. 9 Relationships between $q(X)$

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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