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Distinction of *Push,pull effect* and steric hindrance in disubstituted alkynes

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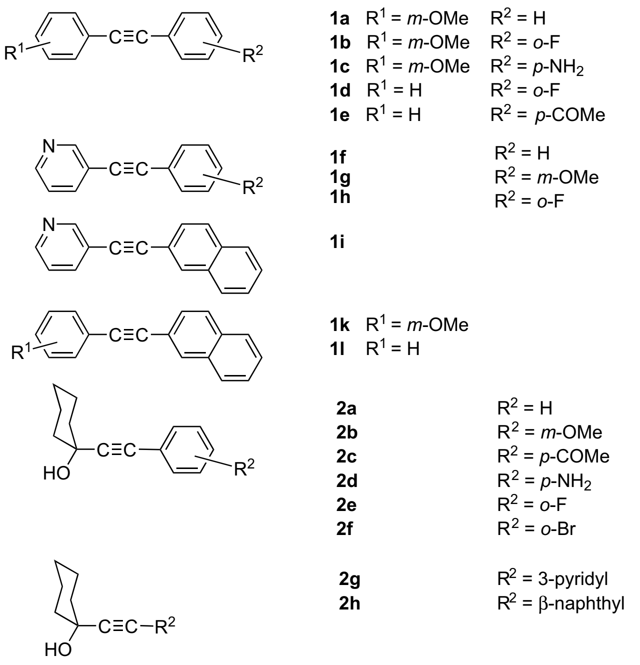
ABSTRACT

The *push,pull effect* in two series of disubstituted alkynes was studied at the DFT level [B3LYP/6-311G(d)] by application of the ^{13}C chemical shift differences (GIAO) between the alkyne carbon atoms ($\Delta\delta_{C\equiv C}$), the charge difference between these carbons ($\Delta q_{C\equiv C}$), the occupation quotient (NBO) of anti-bonding π^*, and bonding π orbitals ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) and the bond length ($d_{C\equiv C}$) of the C≡C triple bond. The linear dependence of $d_{C\equiv C}$ versus $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ quantifies changes in the *push,pull effect* while deviations from the latter correlation indicate and ascertain quantitatively to what extent steric hindrance restricts the strain-less conjugation of the C≡C triple bond π-orbitals in the disubstituted alkynes.

1. Introduction

The *push,pull effect* in substituted alkenes has been quantified by the occupation quotient of anti-bonding π^* and bonding π orbitals of the central C=C double bond ($\pi^*_{C=C}/\pi_{C=C}$).[1,2] As experimental equivalents, (i) the barrier to rotation about the partial double bond $\Delta G^{\#}$,[3] (ii) the ^{13}C chemical shift difference $\Delta\delta_{C=C}$ of the two carbon atoms,[4] and (iii) the corresponding bond length $d_{C=C}$[5] can be employed. Significant limitations, however, restrict general applications [(i) the *push,pull effect* must be extremely high to reduce the partial double bond character sufficiently, (ii) substitution at C=C must be identical, and (iii) exact bond lengths are only available from X-ray studies]. The occupation quotient ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) was successfully applied also for the quantification of the push,pull character in *push,pull alkynes*;[6] as experimental alternatives (with the same limitations mentioned above), $\Delta\delta_{C\equiv C}$ and $d_{C\equiv C}$ were employed,[6] unhindered conjugation between involved orbitals provided. If the latter supposition is not fulfilled, e.g., due to differences in steric hindrance, deviations were observed. The term *push,pull alkynes* was introduced in the literature by Neuenschwander et al.[7]

It is the main topic of this paper to study the steric substituent effect on the intensity of the *push,pull effect* in substituted alkynes. For this purpose two series of substituted alkynes **1** and **2**, recently published by Csékei et al.,[8] were examined (cf. Scheme 1). The



Scheme 1. Compounds studied.

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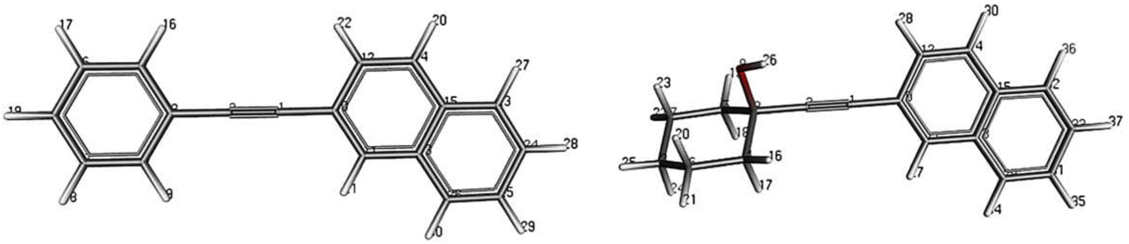

Figure 1. Basic structures of compounds **1l** and **2h** (computed at DFT B3LYP/6-311G* level).

structures of these compounds were computed at the DFT level of theory (B3LYP/6-311G*), chemical shifts at the same level using the GIAO method, and the occupation of relevant orbitals was computed applying an accompanying NBO analysis.[9] Computed *x*,*y*,*z*-coordinates and absolute energies of **1** and **2**, experimental[8] and computed ^{13}C chemical shifts of the C≡C triple bond carbon atoms and their natural charges, and the occupation numbers of C≡C triple bond bonding π and anti-bonding π* orbitals are given as Supplementary data.

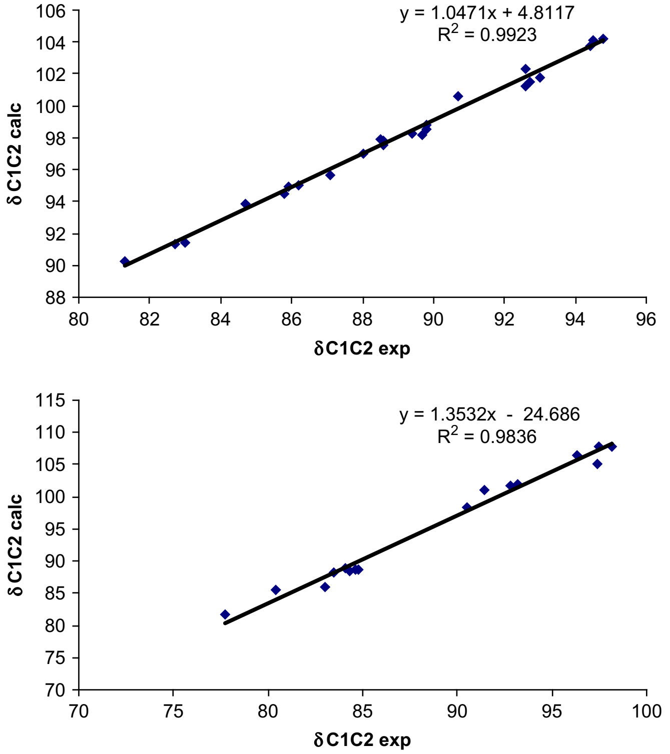

Figure 2. Correlation of experimental[8] and computed ^{13}C chemical shifts of the C≡C triple bond in alkynes **1** (above) and **2** (below).

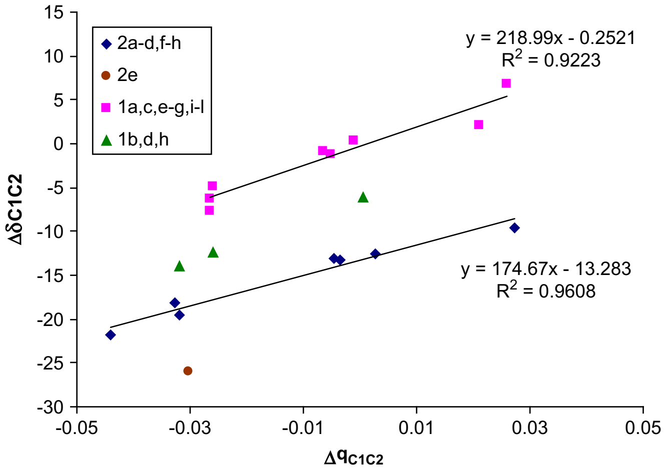

Figure 3. Dependence of computed ^{13}C chemical shift differences of the C≡C triple bond carbon atoms [$\Delta\delta(C^1{\equiv}C^2)$] in alkynes **1** and **2** on differences in charge density of the same carbon atoms [$\Delta q(C^1{\equiv}C^2)$].

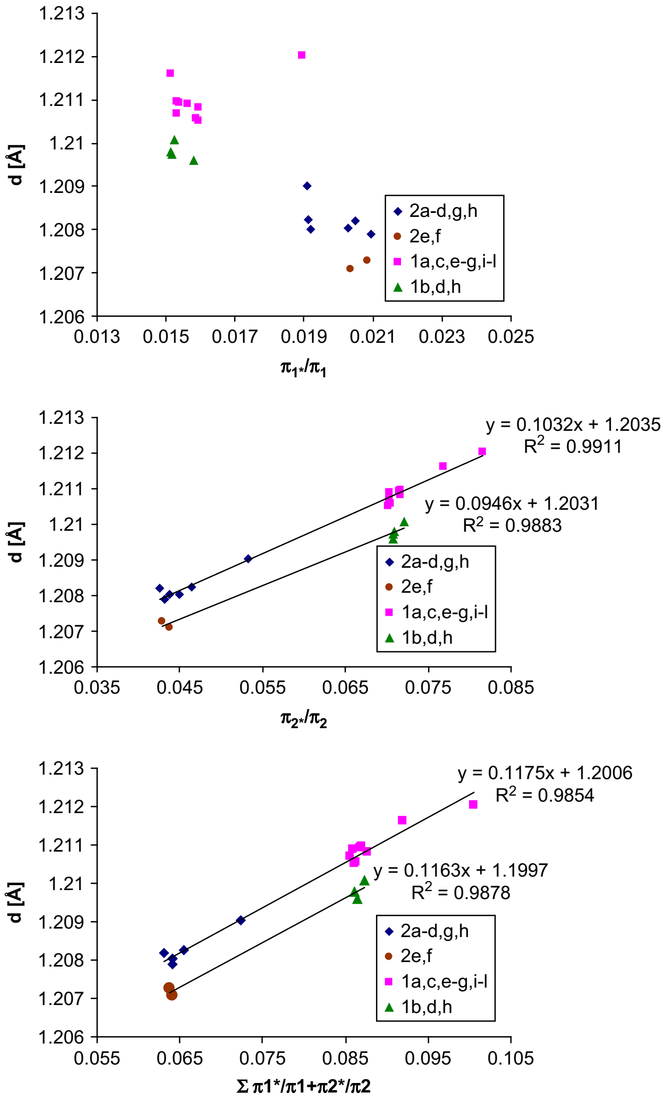

Figure 4. Dependence of the bond length of the C≡C triple bond [$d(C{\equiv}C)$] in alkynes **1** and **2** on the occupation quotients of the anti-bonding π* and bonding π orbitals of this C≡C triple bond.

2. Results and discussion

The basic structures of compounds **1** and **2** are given in Figure 1: the substituted tolanes and naphthyl/pyridyl derivatives **1** prefer planar geometries, the disubstituted cyclohexanes **2** can attain two conformations, ***ax*(OH),*eq*(C≡C)** and ***ax*(C≡C),*eq*(OH)**. Conformer ***ax*(OH),*eq*(C≡C)** proves to be ca. 0.2 kcal mol^{-1} more stable than ***ax*(C≡C),*eq*(OH)** and was further investigated (for 1-ethynylcyclohexanol, the inverted conformer ***ax*(C≡C),*eq*(OH)** was found to be more stable—$\Delta G^{\circ}=-0.55$ to -0.6 kcal mol^{-1}).[15,16] The experimental ^{13}C chemical shifts of **1** and **2**[8] were correlated with the computed values (cf. Fig. 2); excellent agreement [**1**: $\delta(C^1\equiv C^2)_{calcd}=1.0471\,\delta(C^1\equiv C^2)_{exp}+4.8117$ ($R^2=0.9923$); **2**: $\delta(C^1\equiv C^2)_{calcd}=1.3532\delta(C^1\equiv C^2)_{exp}+24.686$($R^2=0.9836$)] was strong evidence for accurate calculated geometries of the compounds studied. Only the computed ^{13}C chemical shifts δ/ppm of the alkyne carbon atoms were employed in the following theoretical study.

For quantifying the *push,pull effect* in alkynes **1** and **2**, the bond length of the C≡C triple bond $d_{C\equiv C}$, the ^{13}C chemical shift difference $\Delta\delta_{C\equiv C}$ (synonymously for charge alternation $\Delta q_{C\equiv C}$), and the occupation quotient of anti-bonding π^* and bonding π orbitals of the C≡C triple bond were applied; barriers to rotation ($\Delta G^{\#}{}_{C\equiv C}$) are not attainable due to the cylindrical π-electron distribution of the C≡C triple bond.

First the causes for the chemical shift difference of the alkyne carbon atoms ($\Delta\delta_{C\equiv C}$) were investigated. This push,pull parameter was correlated to the corresponding charge polarization at the same acetylenic carbon atoms ($\Delta q_{C\equiv C}$) in alkynes **1** and **2** (cf. Fig. 3). Two different linear dependences with nearly the same slopes were obtained [*ortho*-fluoro-substituted tolanes **1b**,**d**,**h**, and **2e**—as outliers]. Thus, it can be concluded that ^{13}C chemical shift differences are similarly dependent on $\Delta q_{C\equiv C}$ (the same slopes), as a measure of the *push,pull effect*, however, for the *o*-F substituted derivatives, there are additional, obviously constant contributions to $\Delta\delta_{C\equiv C}$, which are similar in the two groups of compounds as well. The deviation of **2e** from the best-fit line of other alkynes **2** and that of **1b,d,h** from the correlation obtained for other alkynes **1** is about the same—ca. 5 ppm—and because they are similarly fluoro-substituted, steric hindrance between the fluorine atom and the C≡C triple bond could be the reason (vide infra).

As reason for the different dependences of $\Delta\delta_{C\equiv C}$ versus $\Delta q_{C\equiv C}$ obtained for **1** and **2**, both the anisotropic effect of the aryl substituent in **1**[17] with respect to α-hydroxyl-cyclohexyl in **2** (too small) and the heavy-atom effect (similar in **1** and **2**) are out of question.[18] Obviously, the different volumes of aryl in **1** compared to α-hydroxyl-cyclohexyl in **2** and the π-electron delocalization of the additional aryl substituent in **1** (instead of only the α-hydroxyl-cyclohexyl moiety in **2**) contribute to the stronger ^{13}C chemical shift differences in the α-hydroxyl-cyclohexyl alkynes **2**. To sum up the results of this paragraph, $\Delta\delta_{C\equiv C}$, as a general measure of the active *push,pull effect* in alkynes, can be rejected.

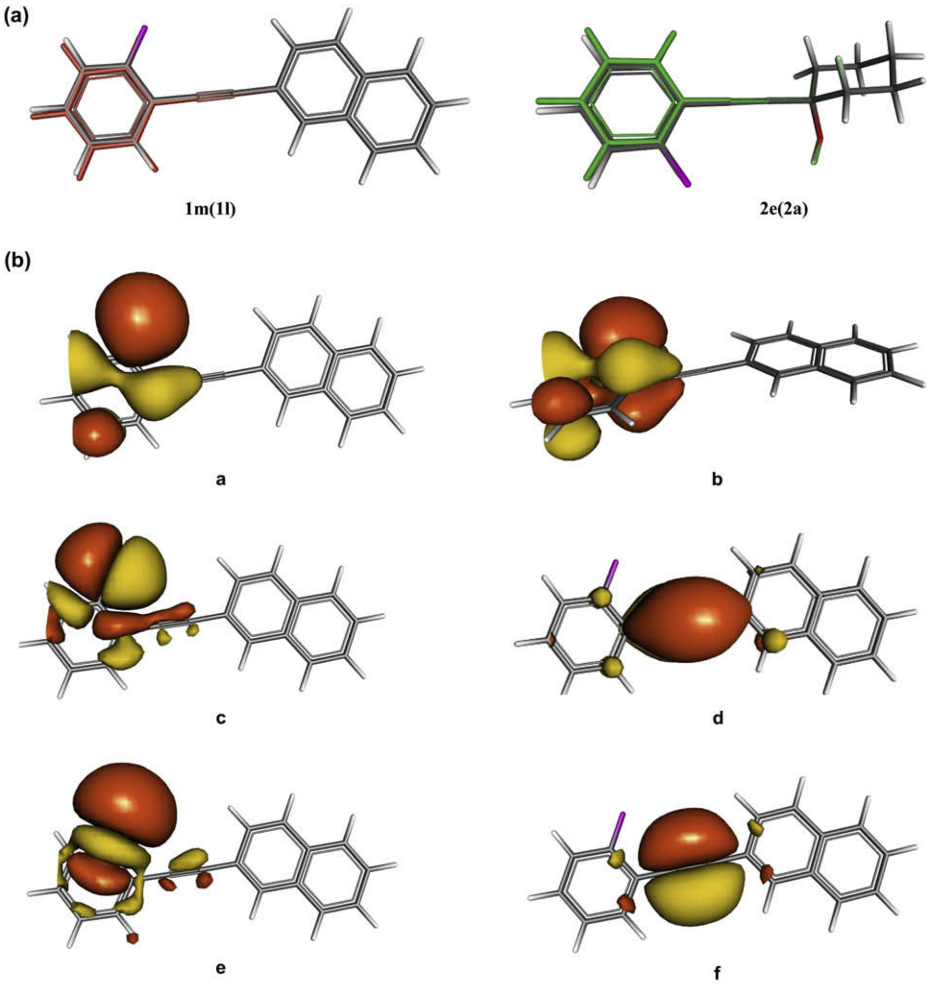

Figure 5. (a) Steric hindrance in the *ortho*-F substituted alkynes **1m** (with respect to **1l**) and **2e** (with respect to **2a**). (b) Depiction of the π orbitals of both the fluoro substituent (a–c) and the C≡C triple bond (d, f) and of the lone pair of the fluoro substituent (e), showing the evident distortion of the orbitals [except of $\pi(1)_{C\equiv C}$ (f)].

Next, the quotient ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) method[1,2,6] was tested for the quantification of the *push,pull effect* in the substituted alkynes **1** and **2**; the corresponding correlations of the bond length $d_{C\equiv C}$ to π^*_1/π_1 (in-plane with substituents), π^*_2/π_2 (perpendicular to the plane of conjugated substituents) and to the sum of the two contributions ($\Sigma\pi^*_1/\pi_1+\pi^*_2/\pi_1$) are given in Figure 4. While the dependence $d_{C\equiv C}$ versus π^*_1/π_1 does not exist (because the conjugation substituent orbitals to π^*_1 and π_1 is prohibited) the remaining two dependences are very similar because π^*_2/π_2 (perpendicular to the plane of conjugated substituents and conjugation permitted) control the dependence and hereby the sum correlation $d_{C\equiv C}$ versus $\Sigma\pi^*_1/\pi_1+\pi^*_2/\pi_1$ as well. In the two correlations two best-fit lines each of about same slope are obtained: on one line **1b,d,h** and **2e,f**, on the second line all other alkynes **1** and **2**. This is a very valuable result excellently characterizing the electronic condition in the alkynes **1** and **2**: restricted conjugation between substituents and π^*_2/π_2 orbitals of the acetylenic C≡C triple bond in the *ortho*-substituted derivatives **1b,d,h** and **2e,f** due to steric hindrance reduces the bond length $d_{C\equiv C}$ by ca. 0.001 Å and the occupation quotient by ca. 0.01. Both steric distortions of the n_F lone pair and π_2 orbitals of the C≡C triple bond as well as expanding of the bond angle ≡C–C(*i*)–C(*o*) (visualized in Fig. 5) corroborate these conclusions.

3. Conclusions

It can be concluded that the occupation quotient (π^*/π) of the anti-bonding $\pi^*{}_{C\equiv C}$ and bonding $\pi_{C\equiv C}$ orbitals of the C≡C triple bond, which are in conjugation with attached substituents, proves to be a unique and general quantitative indication of the *push,pull effect* in substituted alkynes. Additionally, in **1** and **2**, deviations from the best-line of fit of the π^*/π versus the bond length $d_{C\equiv C}$ correlation can be employed to define and clarify the effect of steric hindrance due to *ortho*-flourine substitution on the *push,pull effect* in substituted alkynes, which is shortening of the bond length by ca. 0.001 Å and reducing the occupation quotient by a factor of ca. 0.01.

Supplementary data

Tables of computed *x*,*y*,*z*-coordinates and absolute energies of **1** and **2**, experimental[8] and computed ^{13}C chemical shifts of the C≡C triple bond carbon atoms and their charges, and occupation numbers of C≡C triple bond bonding π and anti-bonding π* orbitals are given. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.075.

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