6774 *J. Phys. Chem. A* **2009,** *113,* 6774–6778

Quantification of the Push−Pull Effect in Substituted Alkynes. Evaluation of ±*I*/±*M* Substituent Effects in Terms of C≡C Bond Length Variation

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Received: March 18, 2009; Revised Manuscript Received: May 2, 2009

^{13}C chemical shifts of alkynes, published to date, were computed at the DFT (B3LYP/6-311G*) level of theory and compared with the experimental δ values, and the agreement was employed as a measure of quality for the underlying structures. For the corresponding global minima structures, thus obtained, the occupation quotients of antibonding π^* and bonding π orbitals ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) and the bond lengths ($d_{C\equiv C}$) of the central C≡C triple bond were computed and correlated to each other. The linear dependence obtained for the two push−pull parameters $d_{C\equiv C}$ and $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ quantifies changes in the push−pull effect of substituents while deviations from the best line of fit indicate and ascertain quantitatively to what extend the inductive (±*I*) substituent effect changes with respect to the bond length of the C≡C triple bond.

1. Introduction

The push−pull effect in substituted alkenes has been quantified by the occupation quotient of antibonding 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 the general applications (for (i), the push−pull effect must be extremely high to reduce the partial double bond character sufficiently, for (ii), substitution at C═C must be identical, and for (iii), exact bond lengths are only available from X-ray studies).

The occupation quotient ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) can be successfully applied also for the quantification of the push−pull character in substituted alkynes;[6] as experimental alternatives, with the same limitations mentioned (vide supra), $\Delta\delta_{C\equiv C}$ and $d_{C\equiv C}$ can be employed,[6] unhindered conjugation between involved orbitals provided. If the latter premise is not ensured, e.g., due to differences in steric hindrance, deviations from the linear dependence $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ vs $d_{C\equiv C}$ were observed[6,7] and employed to quantify present steric hindrance in terms of bond length and the occupation quotient of the central C≡C triple bond. Similar to push−pull alkenes acceptor−donor disubstituted alkynes are characterized as push−pull alkynes; the term was introduced by Neuenschwander et al.[8]

The main topic of this paper was (i) to collect all alkynes where the ^{13}C chemical shifts of the C≡C triple bond carbon atoms are published and (ii) to study the two remaining dependences, $\Delta\delta_{C\equiv C}$ vs $d_{C\equiv C}$ and ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) vs $d_{C\equiv C}$, respectively, with respect to existence and scaling of the push−pull effect in substituted alkynes (the third parameter, $\Delta G^{\#}$, is not available due to the cylindrical π-electron distribution of the C≡C triple bond). The alkynes **1**−**69** of more or less push−pull character could be studied and are given in Scheme 1; the structures were computed at the DFT level of theory (B3LYP/6-311G*), ^{13}C chemical shifts at the same level using the GIAO method, and the occupation of relevant orbitals was computed applying an accompanying NBO analysis.[9] Experimental[15−29] and computed ^{13}C chemical shifts of the C≡C triple bond carbon atoms, the bond length of the C≡C triple bond, and the occupation numbers of C≡C triple bond bonding π and antibonding π^* orbitals of **1**−**69** are given as Supporting Information.

2. Results and Discussion

2.1. $\Delta\delta_{C\equiv C}$/ppm and the Push−Pull Effect in Alkynes. The experimental ^{13}C chemical shifts of **1**−**69** published previously[15−29] were correlated with the computed δ-values (cf. Figure 1); sufficiently good agreement ($\delta(C^1\equiv C^2)_{calc} = 1.0108\ \delta(C^1\equiv C^2)_{exp} + 3.4838$ ($R^2 = 0.9589$; sd = 5.59 ppm) was strong evidence for accurately computed structures of the compounds studied. Only theoretical ^{13}C chemical shifts δ/ppm of the alkyne carbon atoms and bond lengths of the C≡C triple bond were employed in the subsequent study.

First, ^{13}C chemical shift differences $\Delta\delta_{C\equiv C}$/ppm as a measure of the push−pull effect in **1**−**69** were investigated: the corresponding correlation of $\Delta\delta$/ppm vs the bond length of the C≡C triple bond $d_{C\equiv C}$/Å is given in Figure 2. As expected and found for push−pull alkenes,[1,2,4] the correlation is only poor (if there is any) because the ^{13}C chemical shift proves to be dependent on a number of effects,[30] among which the charge polarization due to push−pull substituent effects is only one of them. This result proves the ^{13}C chemical shift difference $\Delta\delta_{C\equiv C}$/ppm of the two alkyne carbon atoms of the C≡C triple bond to be not qualified as a useful indication of the present push−pull character. The situation is not changing if structural variations, altering the push−pull character of the disubstituted alkynes, are less proximate to the alkyne carbon atoms. For this purpose, structurally comparable alkynes (**39**−**50**, **51**−**56**, **57**−**62**, respectively) have been compared (cf. Figure 3); there is no useful correlation as well to corroborate $\Delta\delta$/ppm, the ^{13}C chemical shifts of the C≡C triple bond carbon atoms, as a sensitive parameter to indicate quantitatively the push−pull character of substituted acetylenes.

2.2. Occupation Quotients $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$, $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, $\Sigma\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(2) + \pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$ and the Push−Pull Effect in Alkynes. Thus only the quotient parameter ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) remains to be studied with respect to the C≡C

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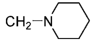
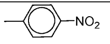
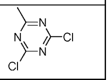
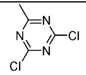
10.1021/jp9024359 CCC: $40.75

SCHEME 1: Compounds Studied

R−C≡C−R′

Compound	R	R′
1	H	H
2	H	Me
3	H	*t*-Bu
4	H	*n*-Pr
5	H	*n*-Bu
6	H	*n*-Hex
7	H	*cyclo*-Prop
8	H	$(CH_2)_2OH$
9	H	
10	H	$CH{=}CH_2$
11	H	$CH{=}CHCH_3$(t)
12	H	$CH{=}CH\text{-}C_2H_5$
13	H	F
14	H	OEt
15	H	SEt
16	H	*n*-Bu
17	H	COMe
18	H	$CONH_2$
19	H	$SiEt_3$
20	H	$SnMe_3$
21	H	$COSi(Ph)Me_2$
22	H	$SiMe_3$
23	H	Si(*t*-Bu)Me_2
24	Me	Me
25	Me	*n*-Pent
26	Me	COMe
27	Me	OMe
28	Me	SO_2Me
29	CH=CH-Me(*t*)	$SiMe_3$
30	CH=CH-Et (*t*)	$SiMe_3$
31	*n*-Pr	*n*-Pr
32	COOMe	COOMe

R−C≡C−R′

Compound	R	R′
33	$SiMe_3$	$SiMe_3$
34	$SnBu_3$	$SnBu_3$
35	SMe	SMe
36	Cl	*n*-Bu
37	SMe	Et
38	SMe	$CH{=}CH_2$
39	NMe_2	CH=CH-CHO
40	NMe_2	CH=CH-COMe
41	N(morpholino)	CH=CH-CHO
42	N(morpholino)	CH=CH-COMe
43	N(Me)Ph	CH=CH-CHO
44	N(piperidino)	CHO
45	N(piperidino)	COMe
46	N(piperidino)	COOMe
47	N(morpholino)	COOMe
48	N(morpholino)	COAryl 
49	NMe_2	COAryl 
50	N(morpholino)	COAryl 
51	CH_2OH	CH=CHCl
52	CH_2OH	CH=CH-*n*-Bu
53	CH_2OH	CH=CH-*cyclo*Hex
54	CH_2OH	CH=CH-Et
55	CH_2OH	CH=CH-*i*-Pr
56	CH_2OH	CH=CHPh
57	$CH(OH)CH_3$	CH=CHCl
58	$CH(OH)CH_3$	CH=CH-*n*-Bu
59	$CH(OH)CH_3$	CH=CH-*cyclo*Hex
60	$C(OH)(CH_3)_2$	CH=CH-Et
61	$C(OH)(CH_3)_2$	CH=CH-*i*-Pr
62	$C(OH)(CH_3)_2$	CH=CHPh

RC≡C−C≡CR′

Compound	R	R′
63	H	H
64	H	Me
65	Me	Me
66	N(morpholino)	$C(Cl){=}C(Cl)_2$

R−C≡C−C≡C−C≡C−R′

Compound	R	R′
67	N(Me)Ph	COOMe
68	N(morpholino)	$C(Cl){=}C(Cl)_2$
69	N(morpholino)	COOMe

triple bond length $d_{C\equiv C}$, and hereby subjected to the present push−pull character in substituted alkynes. In Figure 4, the corresponding dependences of $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$, $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, and $\Sigma\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1) + \pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, respectively, vs $d_{C\equiv C}$ are given. At first glance, all three correlations are not really encouraging; however at a second glance, they make sense.

Contrary to push−pull alkenes, in substituted alkynes, two antibonding π^* and two bonding π orbitals of the C≡C triple bond are available for π-electron delocalization from/to attached substituents, dependent on their ±*M* substituent effects. Hence, both number and orientation of the corresponding substituent orbitals with respect to $\pi^*(1)/\pi(1)$ and $\pi^*(2)/\pi(2)$, respectively, of the C≡C triple bond have to be considered and prove to be crucial for the degree of π-electron delocalization in the compounds studied.

In pent-3-en-1-yne (**11**), for example, the occupation of the $\pi(1)$ orbital (in-plane with the C═C double bond) is negligible compared to $\pi(2)$ which proves to be perpendicular to this plane and can effectively interact and conjugate with the C═C double bond as the substituent; thus, $\pi(1)$ has no influence (cf. Figure 5).

The reversed electronic situation is observed in 2-pentyn-4-one (**26**). The $\pi(1)$ orbital can interact with the π-like orbital of one of the oxygen lone pairs of the C═O double bond while the corresponding $\pi(2)$ orbital of the C≡C triple bond can interact with the π-orbital of the C═O double bond (cf. Figure 5). Hence all π-orbitals of the C≡C triple bond in **26** are involved in the conjugation of π-electron density in the molecule and both paths of conjugation ought to be considered.

Thus, the correlations (i) $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$, (ii) $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, and (iii) $\Sigma\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1) + \pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, respectively, vs $d_{C\equiv C}$ not only provide information about the amount of conjugation of substituents with the various π-orbitals of the C≡C triple bond ((i) and (ii)) but the sum of the two interactions (iii) is related to the push−pull effects in the

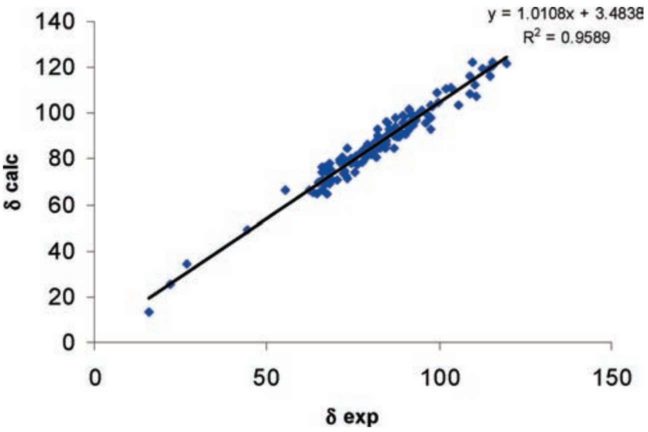


Figure 1. Correlation of experimental[15−29] and computed ^{13}C chemical shifts of the C≡C triple bond carbon atoms in alkynes **1**−**69**.

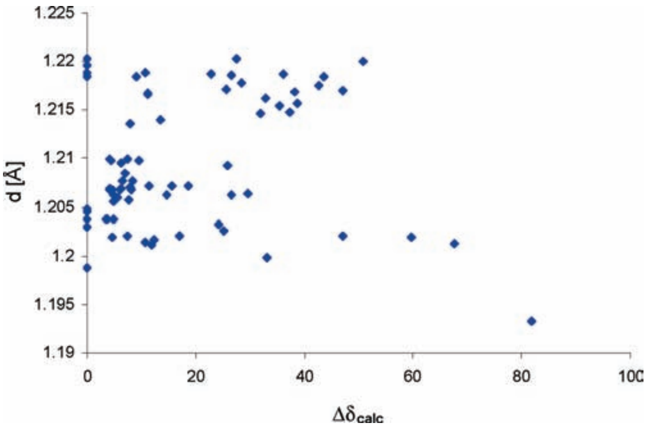


Figure 2. Dependence of ^{13}C chemical shift differences ($\Delta\delta_{C\equiv C}$/ppm) of the C≡C triple bond carbon atoms in alkynes **1**−**69** on the corresponding bond length $d_{C\equiv C}$ of this bond.

substituted alkyne compounds. Within this frame, the correlations given in Figure 4 can be examined.

Because the $\pi(1)$ orbital is (per definition) in plane with most of the substituents (vide supra), there is no acceptable dependence of the C≡C triple bond length $d_{C\equiv C}$ on $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$, except for some outlier substituents (halogens, OR, SO_2R, etc., vide infra) and the trisalkynes **67**−**70**. In the latter compounds, $\pi^*(1)$ and $\pi(1)$ can interact with useful π-orbitals of the adjacent C≡C triple bond. The same is true for the outlier substituents: in addition to π-orbitals, π-like n-orbitals are available for participating in the π-conjugation substituent/C≡C triple bond.

Otherwise the $\pi(2)$ orbital (cf. Figure 4b): the orientation perpendicular to the molecule's plane allows substantial overlap with proximate and useful substituent orbitals and hereby shift of π-electron density. A rough linear dependence $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$ vs $d_{C\equiv C}$ is obtained with a number of readily traceable outliers: above the best-fit line are (i) silicon, phosphorus, and tin substituents and (ii) the trisalkynes **67**−**70**. While the latter group of compounds donate (accept) partial π-electron density into (from) the $\pi^*(\pi)$ orbitals of the adjacent C≡C bond, the former group of outliers lack of lone pairs for π-conjugation. The outlier substituents below the best-fit line incorporate π-like lone pairs for π-conjugation and interact adequately with both $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$ and $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$. In addition, these outliers (F, Cl, SO_2R, OR) are electron-withdrawing substituents which additionally change inductively the C≡C triple bond length and cover hereby the parallel π-conjugation $\pm M$ substituent effects (vide infra).

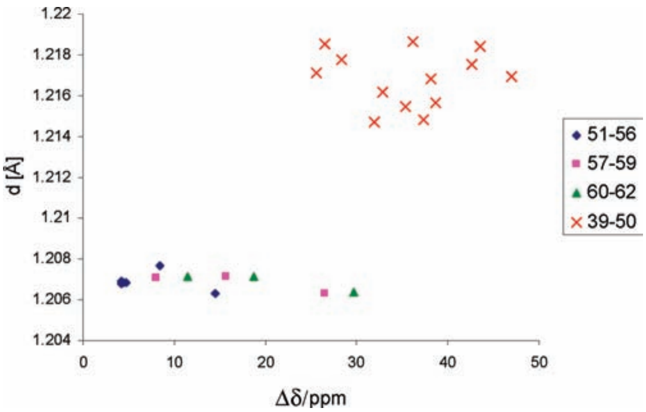


Figure 3. Dependence of ^{13}C chemical shift differences ($\Delta\delta_{C\equiv C}$/ppm) of the C≡C triple bond carbon atoms in alkynes **39**−**62** on the corresponding bond length $d_{C\equiv C}$ of this bond.

The best correlation (cf. Figure 4c) was obtained when adding the $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$ and $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$ contributions: the trisalkynes are now on the best-fit line, above this line are electropositive substituents only which do not take part in the push−pull interactions due to lacking lone pairs and below the best-fit line are only electronegative substituents which take part in the push−pull interactions due to available lone pairs but, due to the additionally existing inductive electron-withdrawing substituent effect, they additionally influence the C≡C triple bond length. The strongest electron-withdrawing substituent fluorine deviates farthest from the best-fit line, as do silicon and tin substituents (as the strongest electropositive substituents) to the other side of this line; higher row halogens and OR substituents at one side, and PR_2 and C(=O)SiR_3 on the other side, exhibit lower inductive electron-withdrawing/electron-donating substituent effects.

2.3. Push−Pull Effect in Terms of Bond Lengths. This is the third multiple bond which was studied by us with respect to the influence of the push−pull effect on the corresponding bond length: the partial C=C and C=N double bonds[2] and now the C≡C triple bond. A rough evaluation of the corresponding Figure 1 in ref 2 and of the corresponding correlation of this study (given in Figure 4c) result in the following changes in bond lengths per change of the occupation quotient by a factor of 0.1

$R_2C{=}CR_2'$	0.04 Å
$R_2C{=}N{-}R'$	0.02 Å
$R{-}C{\equiv}C{-}R'$	0.0125 Å

These changes in bond length are in complete agreement with the reason for this: four substituents, in the case of push−pull olefins, can donate more (accept more) π-electron density into the antibonding π-orbital (from the bonding π-orbital) of the central C=C double bond elongating hereby the bond length of this bond. These possibilities reduce with the availability of three substituents in push−pull imines and two substituents in push−pull alkynes appropriately smaller effects on the corresponding bond lengths.

3. Conclusions

^{13}C chemical shift differences of the C≡C triple bond carbon atoms ($\Delta\delta_{C\equiv C}$/ppm) and the occupation quotients of the antibonding and bonding π-orbitals ($\pi^*_{C\equiv C}/\pi_{C\equiv C}$) of this bond, respectively, were correlated to the C≡C triple bond length $d_{C\equiv C}$

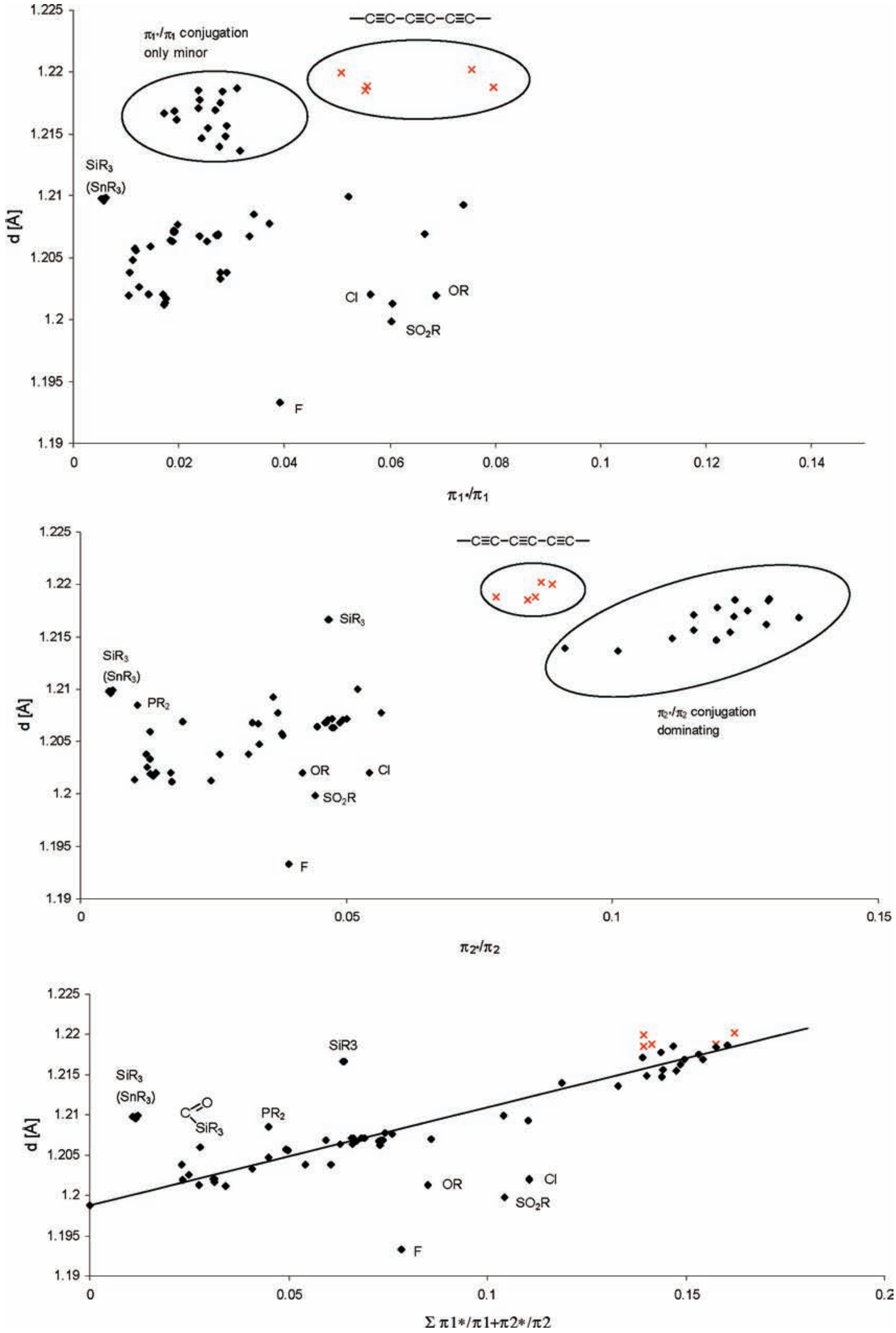
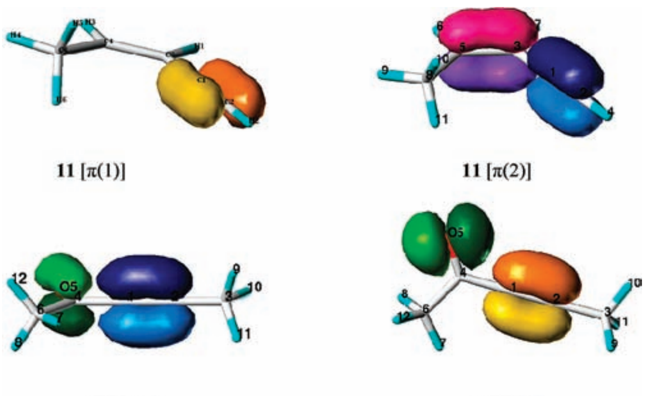


Figure 4. Correlation of occupations quotients $\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$ (top), $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$ (middle), and $\Sigma\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(2) + \pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$ (bottom), respectively, vs $d_{C\equiv C}$.

in order to examine their ability as a sensitive parameter to indicate quantitatively the push−pull substituent effect in substituted acetylenes. While $\Delta\delta_{C\equiv C}$/ppm proves to be useless, the sum of the occupation quotients ($\pi^*_{C\equiv C}(1)/\pi_{C\equiv C}(1)$ and $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$) was found to be a general, sensitive, and quantitative measure of push−pull substituent effects in alkynes. Deviations from the best-line of fit for the push−pull substituent effect can be evaluated quantitatively in terms of additional inductive electron-withdrawing/electron-donating substituent influences.

The occupation quotient $\pi^*_{C\equiv C}(2)/\pi_{C\equiv C}(2)$, a general, quantitative and easily available molecular indicator of the electronic



11 [π(1)] **11** [π(2)]

26 [π(2)] **26** [π(1)]

Figure 5. Visualization of both $\pi(1)$ and $\pi(2)$ of pent-3-ene-1-yne (**11**) and 2-pentyn-4-one (**26**).

properties of push−pull acetylenes can be readily employed for tuning both electronic properties and geometry of, e.g., phenyl acetylene based molecular conductors by changing functional groups.[31,32]

Acknowledgment. The invaluable technical help of Dipl.-Ing. (FH) Sylvia Fürstenberg in preparing the manuscript is gratefully acknowledged.

Supporting Information Available: Experimental and computed ^{13}C chemical shifts of the C≡C triple bond carbon atoms, the bond lengths of the C≡C triple bonds, and the occupation numbers of C≡C triple bond bonding π and antibonding π^* orbitals of alkynes **1**−**69**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Quantum chemical calculations were performed on workstations using the Gaussian 03 software package.[10] DFT calculations were performed at the B3LYP/6-311G* level of theory. The population of the orbitals and lone pairs of **1**−**69** were calculated by NBO analysis[11] and refer to the B3LYP/6-311G* molecular geometries. Chemical shieldings were calculated at the same level of theory using the GIAO method[12,13] and referenced to the TMS shielding value, also calculated at the same level of theory, to obtain chemical shifts. The NBO 5.0 population analysis[11] was used linked to the Gaussian 03 program package[10] with the keywords *POP=NBO READ* for the NBO/NLMO analysis and *plott* for graphical evaluation. The results were graphically illustrated using the program SYBYL.[14]

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JP9024359