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Quantification of the Push−Pull Effect in Tolanes and a Revaluation of the Factors Affecting the ^{13}C Chemical Shifts of the Carbon Atoms of the C≡C Triple Bond

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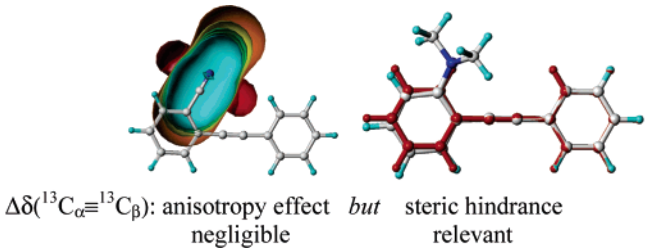

Variously substituted tolanes were employed to show that the *push−pull effect* is also active in C≡C triple bonds by the successful correlation of the occupation quotient π^*/π of the π orbital in resonance with the substituted phenyl moieties of tolanes versus the bond length of the C≡C triple bond. In addition, the influences of the ortho phenyl ring substituents on the ^{13}C chemical shifts of the triple bond carbon atoms, which were estimated by Rubin et al.[4] to be “inapplicable for describing triple bond polarization”, were re-evaluated, leading to the conclusion that, while anisotropic effects of ortho substituents are negligible, the steric *ortho-substituent effects* do in fact dominate the deviations obtained. A detailed theoretical NBO/NCS study has been employed to illuminate the facts of this case.

Introduction

In push−pull alkenes, the *push−pull effect* that is present can be readily quantified by ab initio calculations of the occupation quotient π^*/π of the central C=C double bond.[1] This theoretical quantifiable parameter was proven to be generally useful in substituted alkenes by the examination of a comprehensive set of compounds.[2] If, in asymmetrically substituted alkynes R^1−C≡C−R^2 the substituents R^1 and R^2 are of electron-donating and electron-withdrawing character and are conjugated to the π orbitals of the C≡C triple bond, then the corresponding compounds are analogously termed “push−pull alkynes”.[3] However, to the best of our knowledge, attempts to quantify the corresponding *push−pull effect* in alkynes have not yet been published.

For this purpose and to check for similar dependencies as obtained for push−pull alkenes, a series of substituted tolanes, recently published by Rubin et al.,[4] were examined. These authors[4] also employed the ^{13}C chemical-shift difference of the ethyne carbon atoms for an assessment of the electronic polarization of the C≡C triple bond, as we had done previously for characterizing push−pull alkenes.[5,6] Though they found this parameter, $\Delta\delta_{C\equiv C}$, to be very useful for the para-substituted tolanes, it did not appear, however, to be applicable to the corresponding ortho-substituted analogues. The reason proffered by the authors for this anomaly,[4] magnetic anisotropies stemming from the ortho substituents, is questioned in the present study, and the *ortho-substituent effects* are carefully reevaluated by a detailed theoretical NBO/NCS study.

Results and Discussion

Quantification of the Push−Pull Effect in Tolanes. The polarization of the central partial C=C double bond of push−

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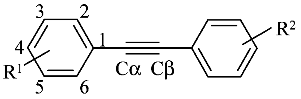
10.1021/jo060199j CCC: $33.50

CHART 1



Compound	R^1	R^2	Compound	R^1	R^2
1a	H	H			
1b	p-Me	H	**2b**	o-Me	H
1c	p-OMe	H	**2c**	o-OMe	H
1d	p-NMe_2	H	**2d**	o-NMe_2	H
1e	p-F	H	**2e**	o-F	H
1f	p-CF_3	H	**2f**	o-CF_3	H
1g	p-CN	H	**2g**	o-CN	H
1h	p-COMe	H	**2h**	o-COMe	H
3b	m-Me	H	**4b**	o-OMe	p-OMe
3c	m-OMe	H	**4c**	o-OMe	p-CN
3d	m-NMe_2	H	**4d**	o-OMe	p-COMe
3e	m-F	H	**4e**	o-OMe	p-COOMe
3f	m-CF_3	H	**4f**	o-OMe	p-CF_3
3g	m-CN	H	**4g**	o-OMe	p-Me
3h	m-COMe	H	**4h**	o-OMe	p-F
			4i	o-OMe	p-NMe_2
5b	o-CN	p-F	**6b**	o-Me	p-F
5c	o-CN	p-Me	**6c**	o-Me	p-Me
5d	o-CN	p-CF_3	**6d**	o-Me	p-CF_3
5e	o-CN	p-NMe_2	**6e**	o-Me	p-NMe_2
5f	o-CN	p-COMe	**6f**	o-Me	p-COMe
5g	o-CN	p-OMe	**6g**	o-Me	p-OMe
5h	o-CN	p-CN	**6h**	o-Me	p-CN

pull alkenes, as a result of the presence of the *push−pull effect*, has, in the past, been quantified by a number of experimental parameters: (i) the barrier to rotation about the partial double bond, $\Delta G^{\#}$,[7] (ii) the ^{13}C chemical-shift difference, $\Delta\delta_{C=C}$, of the two carbon atoms,[8] and (iii) the corresponding bond length, $p_{C=C}$.[9] However, all of them have significant limitations. 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 to observe explicitly only electronic effects, the substitutions must be sufficiently distant; and for (iii), exact bond lengths are only available from X-ray studies. Thus, a general, easy-to-implement experimental parameter to quantify the push−pull effect is not available for all cases. To alleviate this shortcoming, theoretical calculations have been employed and from which the orbital occupation coefficient $\pi^*_{C=C}/\pi_{C=C}$ was found to be satisfactory for this purpose.[1] In the case of asymmetrically disubstituted alkynes, the barrier to rotation is not assessable due to the cylindrical π-electron distribution of the ethyne moiety, but the ^{13}C chemical-shift difference of the sp carbon atoms, $\Delta\delta_{C\equiv C}$, has been used to estimate the π-bond polarization.[10] Deviations from the corresponding linear correlations, $\Delta\delta_{C\equiv C}$ versus $\Delta q_{C\equiv C}$ (electron density difference surrounding the probe nuclei), in the case of ortho-substituted tolanes were interpreted initially as an inverse polarization of the C≡C triple bond[11] and later as magnetic anisotropy influences of the ortho substituents, which should make ^{13}C NMR data inapplicable for ascribing the triple-bond polarization.[4] This parameter, $\Delta\delta_{C\equiv C}$, was also employed to quantify the effect of the coordination of alkynes to cobalt.[12] However, to the best of our knowledge, employing the orbital occupation coefficient $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ for the evaluation of the *push−pull effect* in alkynes has not yet been attempted.

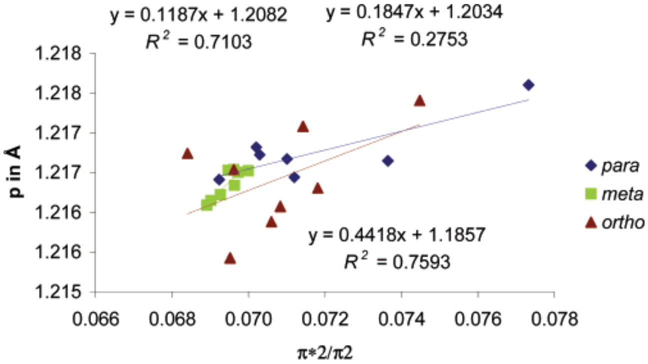


FIGURE 1. Correlation of $p_{C\equiv C}$ and occupation quotient $\pi 2^*_{C\equiv C}/\pi 2_{C\equiv C}$ in monosubstituted tolanes **1**−**3**.

Three series of monosubstituted tolanes (para, **1**, ortho, **2**, and meta, **3**) and three series of push−pull tolanes (**4**−**6**, cf. Chart 1) were theoretically calculated by DFT at the B3LYP/6-31G*[13] level of theory, and the occupations of the relevant orbitals and their interactions were studied by a detailed NBO analysis;[14] the results are presented in Tables S1 (compounds **1**−**3**) and S2 (compounds **5** and **6**) in the Supporting Information. The corresponding bond lengths of the central C≡C triple bond ($p_{C\equiv C}$) are also included in Tables S1 and S2 in the Supporting Information. Neither the bond lengths nor the occupations of the π orbitals of the triple bond change strongly, but significantly, this is not unexpected, because the site of substitution is quite removed from the ethyne bond. Even for ortho substitution, this modification is still three bonds distal. Additionally, only one of the two π orbitals is included in the orbital interactions, thus limiting the effect.

If the monosubstituted tolanes are considered first, the trend is clear-cut (cf. Figure 1): increasing polarization of the triple bond, evident by rising occupation quotients, $\pi 2^*_{C\equiv C}/\pi 2_{C\equiv C}$, increases the bond length of the triple bond concomitant with lower triple-bond character. Obviously, this behavior reflects the behavior expressed by push−pull alkenes,[1,2] where the occupation number of the bonding π orbital of the central C≡

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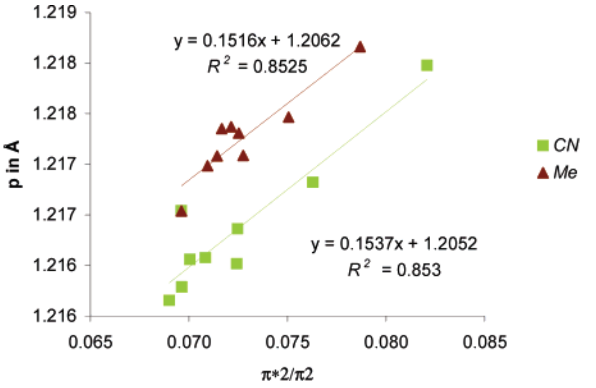

FIGURE 2. Correlation of $p_{\mathrm{C}\equiv\mathrm{C}}$ and occupation quotient $\pi 2^*_{\mathrm{C}\equiv\mathrm{C}}/\pi 2_{\mathrm{C}\equiv\mathrm{C}}$ in disubstituted tolanes **5** and **6**.

C triple bond, in resonance with the substituents, quantitatively describes the acceptor power of the substituents and the corresponding occupation number of the antibonding π^* orbital, also in resonance, and the donor power of the substituents. The correlation for compounds **1**−**3** grouped together, however, is rather poor ($R^2 = 0.4872$), but if the different groups are examined separately, then the correlations improve (cf. Figure 1). In the cases of meta- and para-substituted tolanes, the within-series correlations are fine, and the only unacceptable correlation is for the ortho-substituted series (compounds **2**). Obviously, there is an additional effect (an *ortho-substituent effect*, usually of steric influence, vide infra), which prevents similar successful dependencies, as obtained for the meta and para analogues. Of worthy note, the occupation quotient of the second π orbital, $\pi 1^*_{\mathrm{C}\equiv\mathrm{C}}/\pi 1_{\mathrm{C}\equiv\mathrm{C}}$, perpendicular to the former one, does not change at all because it is not in resonance with the two phenyl rings.

The poor correlation obtained in the case of the ortho-substituted tolanes **2** infers the presence of an additional substituent effect. For this reason, another two sets of push−pull tolanes **5** and **6** were studied (results in Table S2 in the Supporting Information and the correlations of $\pi 2^*_{\mathrm{C}\equiv\mathrm{C}}/\pi 2_{\mathrm{C}\equiv\mathrm{C}}$ vs $p_{\mathrm{C}\equiv\mathrm{C}}$ portrayed in Figure 2). As a result of the push−pull effect, the triple-bond polarization increases and two dependencies of approximately the same gradient are obtained. This result is in complete agreement with our suggestion of different steric situations in the two different series of compounds **5** and **6** (vide infra); in the case of **5**, steric hindrance is the smaller one, and the *push−pull effect* of the para substituent in the other phenyl ring proved to be larger in the variety of both occupation quotient and bond length compared with the corresponding *push−pull effect* in the second series **6** with a methyl substituent in the ortho position. The steric effect of methyl is higher, thereby reducing the two parameters which quantify the *push−pull effect*. These results unambiguously prove that the *push−pull effect* in substituted tolanes can be quantified by both the occupation quotient, $\pi 2^*_{\mathrm{C}\equiv\mathrm{C}}/\pi 2_{\mathrm{C}\equiv\mathrm{C}}$, *and* the bond length, $p_{\mathrm{C}\equiv\mathrm{C}}$, of the triple bond. These parameters are also applicable to ortho-substituted tolanes if the different steric effects of the ortho substituents are handled appropriately.

Ab initio MO Calculation of the Anisotropic Effect of ortho Substituents in Tolanes 2. Recently, Klod and Kleinpeter[15] reported the ab initio MO calculations of the anisotropic effects of a number of functional groups and the ring current effect of aromatic/heteroaromatic moieties. The magnetic anisotropies of substituents can be visualized as isochemical shielding surfaces (ICSS), and examples are depicted in Figure 3. Only minor influences from the anisotropic effects of the ortho substituents on the triple-bond carbons could be found: 0.2 to

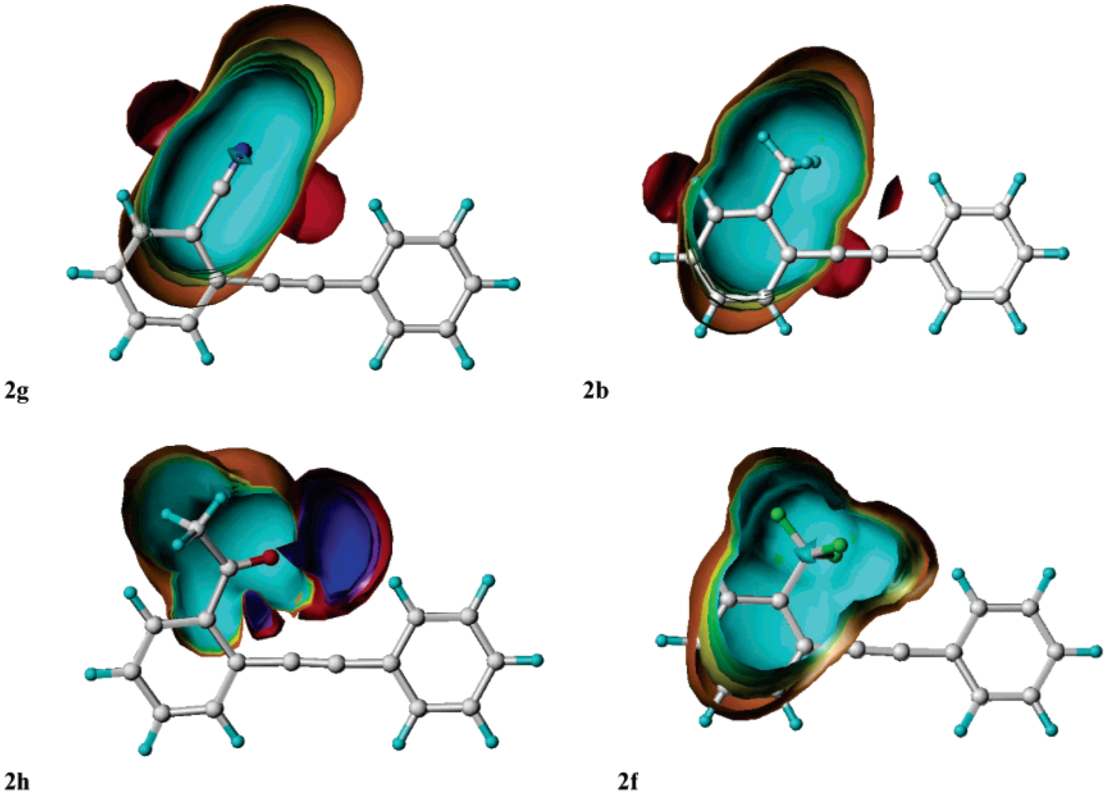
2g **2b**
2h **2f**

FIGURE 3. Preferred conformers of **2b**,**f**−**h** and calculated anisotropic effects of *o*-Me, *o*-CF$_3$, *o*-CN, and *o*-COMe substituents, respectively, on the carbons of the triple bond. The orange ICSS represent shieldings of −0.1 ppm.

TABLE 1. NCS Analysis of Tolanes 1a and 2g with Consideration to the Partitions of *o*-CN on the Triple-Bond Carbon Atoms

								(L + NL)	(L + NL)	(L + NL)	(L + NL)	$\Delta\sigma$	$\Delta\sigma$
bond		**1a**, C-α	**1a**, C-β	**2g**, C-α	**2g**, C-β	$\boldsymbol{\Delta\sigma}$, C-α	$\boldsymbol{\Delta\sigma}$, C-$\beta$	**1a**, C-α	**1a**, C-β	**2g**, C-α	**2g**, C-β	**1a−2g**, C-α	**1a−2g**, C-β
C2−H8 (C8)	L	−1.17	−0.23	0.74	0.17	1.91	0.40	−0.80	0.27	0.85	0.41	−1.65	−0.14
	NL	0.37	0.50	0.11	0.24	−0.26	−0.26						
C8−N10	L			−0.28	−0.10	−0.28	−0.10			−0.02	0.06	0.02	−0.06
	NL			0.26	0.16	0.26	0.16						
C8−N10	L			−0.74	−0.37	−0.74	−0.37			−0.32	−0.23	0.32	0.23
	NL			0.42	0.14	0.42	0.14						
C8−N10	L			0.14	0.08	0.14	0.08			0.38	0.05	−0.38	−0.05
	NL			0.24	−0.03	0.24	−0.03						
N10(lp)	L	0.00	0.00	−1.16	−1.09	−1.16	−1.09	0.00	0.00	−0.46	−0.35	0.46	0.35
	NL	0.00	0.00	0.7	0.74	0.70	0.74						
Σ(NCS)												−1.23	0.33
$\sigma_{\text{calc.}}$												−3.99	7.55
$\delta_{\text{exp.}}$												3.82	−6.52

−0.15 ppm on C-α and −0.05 to −0.09 ppm on C-β. Without doubt, these values are far too small to serve as an explanation for the inapplicability of $\Delta\delta_{C\equiv C}$ to describe bond polarization in ortho-substituted tolanes, as has been recently suggested.[4]

Steric Hindrance in ortho-Substituted Tolanes 2. Following the gage invariant atomic orbital (GIAO) calculation of the ^{13}C chemical shifts of the triple-bond carbon atoms in **2d**, **2g**, and, for comparison to an unsubstituted tolane, **1a**, the theoretical NMR shieldings of C-α and C-β in these three compounds were partitioned into magnetic contributions from the various bonds and lone pairs present in the structures by employing NCS analysis[16] based on the NBO method.[14] Both localized (Lewis) and nonlocalized (non-Lewis) contributions to the shieldings of C-α and C-β in **2d**, **2g**, and **1a** were calculated and are presented in Tables S3 and S4 in the Supporting Information. However, for the purposes of this discussion only the net magnetic partitions of each particular bond to the NCS of C-α and C-β need actually be considered, that is, not only are the Lewis and non-Lewis components summed, but also the total contributions of multiple bonds.

An excellent reproduction of the experimental chemical-shift differences between C-α and C-β in **2d** and **2g** compared with those of **1a** was obtained by these GIAO calculations: *o*-CN, C-α [$\Delta\delta_{\text{exp}} = -3.82$ ppm, $\Delta\sigma_{\text{calc}} = 3.99$ ppm (deshielding: δ scale, positive sign; σ scale, negative sign)] and C-β ($\Delta\delta_{\text{exp}} = 6.52$, $\Delta\sigma_{\text{calc}} = -7.55$ ppm); *o*-NMe$_2$, C-α ($\Delta\delta_{\text{exp}} = -0.49$ ppm, $\Delta\sigma_{\text{calc}} = 0.10$ ppm) and C-β ($\Delta\delta_{\text{exp}} = 5.32$, $\Delta\sigma_{\text{calc}} = -5.29$ ppm). Thus, C-α is shifted to higher and C-β to lower field, and both results are consistent with γ and δ effects in ^{13}C NMR that result in resonances being shifted to different directions, even though steric strain is the underlying source in both cases.[17] It is notable that while the mechanism responsible for the shielding of the γ effect is well-understood,[18−20] the mechanism responsible for the deshielding arising from the δ effect is still under discussion.[21]

Although to some degree all of the bonds in the ortho-substituted tolanes contribute to the NCS of the triple-bond carbon atoms in their respective structures, only a few bonds are of significance (cf. Tables S3 and S4 in the Supporting Information), especially in consideration of those partitions that result in the chemical-shift differences between **2d**, **2g**, and **1a**. Careful examination of these crucial bonds that contribute to the chemical-shift differences revealed some interesting features.

For the contributions to the NCS of C-α and C-β, only the bonds directly associated with the $C_\alpha \equiv C_\beta$ system (C_α−C_1, C_1−C_2, and C_2-ortho-substituent) are significant. Quite a large contribution comes from the ortho substituents, for example, C−α, −1.23 ppm (*o*-CN) and 0.74 ppm (*o*-NMe$_2$) and C-β, 0.33 (*o*-CN) and 1.29 ppm (*o*-NMe$_2$), see for comparison Tables 1 and 2. The corresponding partitions to the NCS of C-α and C-β for the corresponding para substituents were also calculated and found to be negligible (see the Supporting Information for a full listing for all compounds). Thus, both the contributions to NCS of bonds/lone pairs directly associated with the triple bond and the different partitions of the ortho substituents are unequivocal indications[22] for steric hindrance arising from the γ/δ-fragments that are present and, in addition, that the extent of steric hindrance for the γ/δ-fragments was subject to the particular ortho substituent that was present.

The inference of steric interaction with the γ/δ-fragments in **2d** and **2g** in comparison to **1a** is conveyed by the chemical shifts of the corresponding carbon atoms and which is further supported by the structural distortions present in the geometry-optimized structures of the ortho-substituted tolanes **2** (cf. Table 3). For example, the C_1−C_α and $C_\alpha \equiv C_\beta$ bonds are significantly shortened, while the adjacent C_1−C_2 and C_2−C_3 bonds are lengthened in agreement with considerable steric compression being experienced within the γ/δ moieties of **2**. Furthermore, the bond angles C_1−C_2−R^1 and C_2−C_1−C_α are all increased (up to 3.5°, cf. Table 3), again in line with the greater strain experienced by **2**, and the bond angle C_2−C_3−H_3 is correspondingly reduced to compensate for the steric hindrance in the ortho fragments in **2**. Thus, overall structures of **2** are widened and opened up in comparison to the structure of **1a**. In the case of **2d**, the steric hindrance is so great that, in addition, even the dihedral angle R^1−C_2−C_1−C_α is twisted by 3°, and this contrast is visualized in Figure 4, where global minima structures of **1a** and **2d** are compared.

Two items remain to be mentioned. First, in the case of **2e** (*o*-F), opposite structural effects were observed to those expected (cf. Table 3) given that fluorine is larger than hydrogen, and thus the indication of less steric strain compels one to conclude

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TABLE 2. NCS Analysis of Tolanes 1a and 2d with Consideration to the Partitions of *o*-NMe$_2$ on the Triple-Bond Carbon Atoms

bond		**1a**, C-α	**1a**, C-β	**2d**, C-α	**2d**, C-β	**Δσ**, C-α	**Δσ**, C-β	(L + NL) **1a**, C-α	(L + NL) **1a**, C-β	(L + NL) **2d**, C-α	(L + NL) **2d**, C-β	Δσ **1a−2d**, C-α	Δσ **1a−2d**, C-β
N10(lp)	L	0.00	0.00	−0.96	−0.59	−0.96	−0.59	0.00	0.00	−0.50	−0.57	0.50	0.57
	NL	0.00	0.00	0.46	0.02	0.46	0.02						
N8−C10	L	0.00	0.00	0.27	0.14	0.27	0.14			0.21	0.08	−0.21	−0.08
	NL	0.00	0.00	−0.06	−0.06	−0.06	−0.06						
N8−C26	L	0.00	0.00	−0.16	−0.10	−0.16	−0.10			−0.17	−0.11	0.17	0.11
	NL	0.00	0.00	−0.01	−0.01	−0.01	−0.01						
C10−H27	L	0.00	0.00	0.09	0.04	0.09	0.04			0.05	0.00	−0.05	0.00
	NL	0.00	0.00	−0.04	−0.04	−0.04	−0.04						
C10−H28	L	0.00	0.00	−0.66	−0.49	−0.66	−0.49			−0.37	−0.63	0.37	0.63
	NL	0.00	0.00	0.29	−0.14	0.29	−0.14						
C10−H29	L	0.00	0.00	0.08	−0.05	0.08	−0.05			0.04	−0.06	−0.04	0.06
	NL	0.00	0.00	−0.04	−0.01	−0.04	−0.01						
Σ(NCS)												0.74	1.29
$\sigma_{\mathrm{calc.}}$												0.10	5.29
$\delta_{\mathrm{exp.}}$												0.49	−5.32

TABLE 3. Geometry Parameters of Tolanes 1a and 2 Subjected to the ortho-Substituent Effect

first atom of R^1, substituent	H, **1a**	Me, **2b**	OMe, **2c**	NMe$_2$, **2d**	F, **2e**	CF$_3$, **2f**	CN, **2g**	COMe, **2h**
R^1−C$_2$−C$_1$	119.18	120.65	115.70	120.32	118.64	120.18	120.09	121.21
C$_2$−C$_1$−C$_\alpha$	120.54	120.60	120.73	122.36	120.91	121.95	120.66	124.08
R^1−C$_2$−C$_3$	120.48	121.02	124.36	121.77	118.85	119.68	119.58	120.20
C$_2$−C$_3$−H$_9$	119.63	118.83	120.45	119.48	119.03	119.19	119.05	119.35
R^1−C$_2$−C$_1$−C$_\alpha$	0.00	0.00	0.00	−3.00	0.00	0.00	0.00	0.00
R^1−C$_2$−C$_3$−H$_9$	0.00	0.00	0.00	−2.40	0.00	0.00	0.00	0.00
C$_2$−C$_1$	1.409	1.419	1.420	1.428	1.406	1.417	1.422	1.425
C$_2$−C$_3$	1.393	1.397	1.398	1.405	1.387	1.394	1.402	1.404
C$_3$−H$_9$	1.087	1.087	1.084	1.084	1.085	1.084	1.085	1.085
C$_1$−C$_\alpha$	1.426	1.425	1.422	1.424	1.421	1.422	1.419	1.421
C$_\alpha$≡C$_\beta$	1.217	1.217	1.216	1.217	1.216	1.215	1.216	1.217

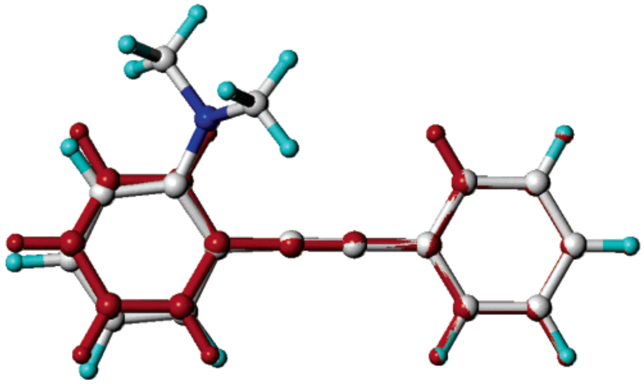

FIGURE 4. Overlaid geometry-optimized structures of **1a** (red framework) and **2d**.

that attractive interactions within this γ fragment are present.[23] Second, it is abundantly clear that none of these effects are evident in the meta- and para-substituted analogues **1** and **3**.

This structural evidence for the presence of considerable strain in **2** extends to distortions that are also apparent in the $\pi 2_{\mathrm{C}\alpha-\mathrm{C}\beta}$ orbital and the $\sigma_{\mathrm{C-H}}$ orbitals of the ortho substituent and which are depicted in Figure 5 for the example compound **2b**. These structural perturbations clearly indicate the presence of great steric strain, which undoubtedly must have an influence on the chemical shifts of the ethyne carbon atoms from these γ/δ fragments and which must, therefore, be accounted for. Distortions of the π cloud have already been reported previously by Martin et al.[24,25] together with short distances to one methine proton positioned above the π systems in supermolecules, thus supporting the suggestion of van der Waals orbital compression effects.

Polarization of the C$_\alpha$≡C$_\beta$ Triple Bond, Natural Charges, and ^{13}C Chemical Shifts of C$_\alpha$ and C$_\beta$. The charge densities at the triple-bond carbons in tolanes **1**−**6** were closely examined because the corresponding ^{13}C chemical shifts were previously found[4] not to be useful for deducing the electronic polarization of the triple bond. Table S5 in the Supporting Information collects the natural charges and charge differences between C-α and C-β and, in addition, the ^{13}C chemical-shift differences between C-α and C-β; the latter two parameters are correlated to each other, and the dependencies are visualized in Figure 6. While para- and meta-substituted tolanes **1** and **3** show excellent linear dependencies, this is not the case for the ortho series **2**, these results having already been obtained by Rubin et al.[4] For the push−pull tolanes **4**−**6** (calculated results are presented in Table S6 in the Supporting Information and correlations are presented in Figure 7), excellent correlations for $\Delta\delta_{\mathrm{C}\alpha-\mathrm{C}\beta}$ versus $\Delta q_{\mathrm{C}\alpha\equiv\mathrm{C}\beta}$ are obtained. Three different dependencies are obtained for the three different types of push−pull alkynes (*o*-OMe, **4**, *o*-CN, **5**, and *o*-Me, **6**), but all have approximately the same gradient and are, thus, only vertically shifted. The conclusion from this result is clear: identical dependencies of $\Delta q_{\mathrm{C}\alpha\equiv\mathrm{C}\beta}$ versus $\Delta\delta_{\mathrm{C}\alpha-\mathrm{C}\beta}$ subject to the variation of the para substituents in **4**−**6** remain in place, but the steric conditions (vide supra) are different in the three groups of push−pull tolanes. The steric differences can actually be quantified by the value of b from the relationship $\Delta q_{\mathrm{C}\alpha\equiv\mathrm{C}\beta} = a \times \Delta\delta_{\mathrm{C}\alpha-\mathrm{C}\beta} + b$ and which provides values of about 1 ppm in the case of *o*-CN, **5**, about

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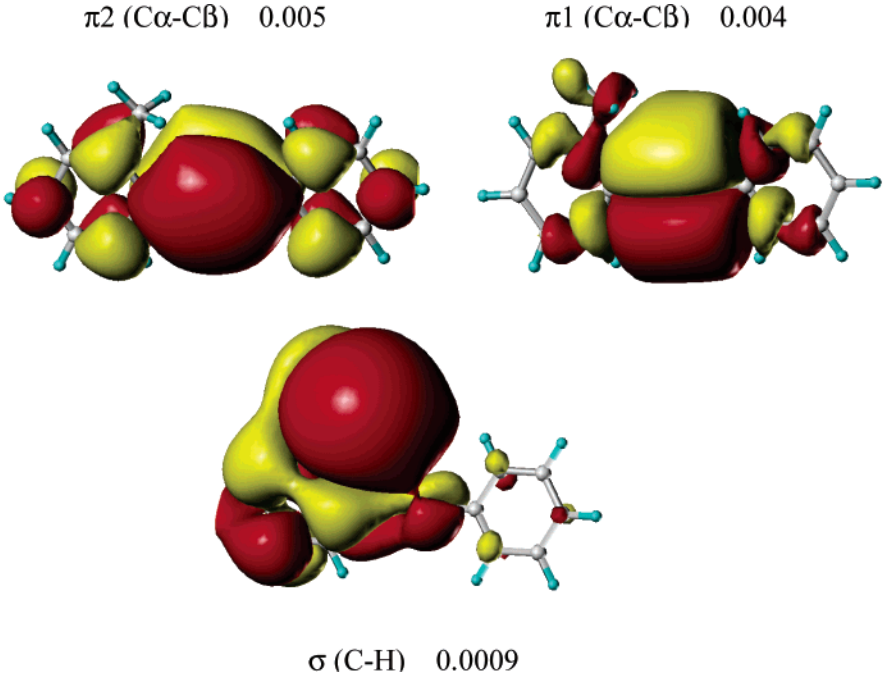

FIGURE 5. Depiction of the $\pi 2_{C\alpha\equiv C\beta}$ and σ_{C-H} orbitals of **2b**, clearly showing the evident distortion of the orbitals as a result of steric interaction.

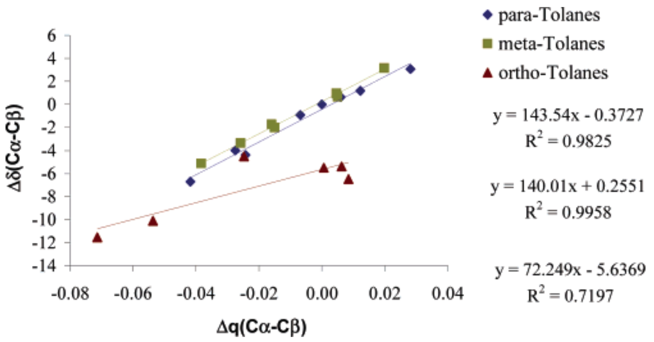

FIGURE 6. Correlation of charge polarization and ^{13}C chemical-shift difference in tolanes **1**−**3**.

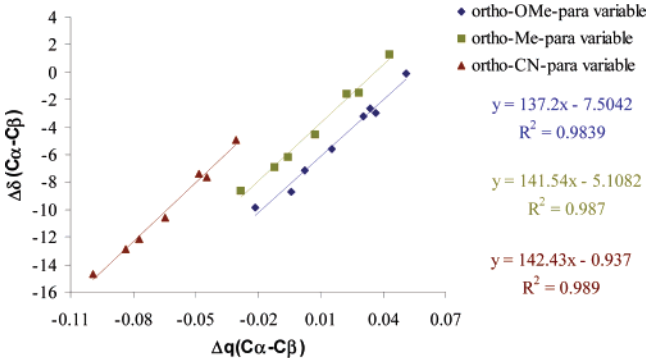

FIGURE 7. Correlation of charge polarization and ^{13}C chemical-shift difference in tolanes **4**−**6**.

5 ppm in the case of *o*-Me, **6**, and about 7.5 ppm in the case of *o*-OMe analogues, **4**. (For meta- and para-substituted tolanes **1** and **3**, the value of *b* is near to zero, +0.25, and −0.37 ppm, respectively, cf. Figure 6.) Thus *b* is quantitatively the steric *ortho-substituent effect* in terms of the ^{13}C chemical-shift difference in the corresponding ortho-substituted tolanes.

Conclusions

The polarization of the C≡C triple bond of tolanes is described well by the ^{13}C chemical-shift difference, $\Delta\delta_{C\alpha-C\beta}$, of carbon atoms constituting the triple bond.[4] Deviations from linearity in the case of ortho-substituted tolanes are not a result of the magnetic anisotropic effects of the ortho substituents,[4] but rather, a result of steric hindrance arising from the γ/δ fragments of the compounds incorporating the ortho substituents. Aside from the steric peculiarities of the ortho-substituted tolanes, $\Delta\delta_{C\alpha\equiv C\beta}$ also proved to be an excellent parameter to quantify the *push*−*pull effect* in tolanes. Both the bond length of the C≡C triple bond and the π electron occupation quotient $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ of the π orbital in resonance with the substituted tolane phenyl moieties were also found to be equivalent parameters in this respect. These parameters for describing the *push-pull effect* will probably not be limited to tolanes, but will likely be applicable to the evaluation of all asymmetrically disubstituted alkynes. Corresponding studies are underway in this regard.

Experimental Section

Quantum chemical calculations were performed on workstations using the Gaussian 03 software package.[13] DFT calculations were made at the B3LYP/6-31G* level of theory. The population of the atoms and lone pairs of tolanes **1**−**6** were calculated by NBO analysis[14] and refer to the B3LYP/6-31G* molecular geometries. Chemical shieldings were calculated at the same level of theory using the GIAO method[26,27] and referenced to TMS shielding values, also calculated at the same level of theory, to obtain chemical shifts. The NBO 5.0 population analysis[14] was used linked to the Gaussian 98 program package[13] with the keywords *POP*=*NBO READ* for the NBO/NLMO analysis and *plott* for graphical evaluation. NCS analysis was performed within the NBO 5.0 population analysis

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with *nrt* and *nrtthr* = 10. The results were graphically illustrated using the program SYBYL.[28] The NCS/NBO analyses partitioned quantitatively the shielding of a particular nucleus into magnetic contributions from all bonds and lone pairs in the structures, with the shielding and deshielding contributions being divided into Lewis and non-Lewis components.

The anisotropic effects of C≡N, Me, COMe, and CF_3 (chemical shieldings as NICS in the surroundings of the molecules) were calculated as described in ref 15. Within the SYBYL contour file, the anisotropic effects of the functional groups under investigation were visualized as ICSS, enabling appreciation of the spatial extension of the anisotropy effect to particular nuclei.

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Supporting Information Available: Natural chemical shieldings, coordinates, absolute energies, and natural charges for the nuclei of tolanes **1**−**6** at the B3LYP/6-31G* level of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) *SYBYL*, version 6.9; Tripos, Inc.: St. Louis, MO, 2003.