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π-Delocalization in Oligoalkynes Induced by Push−Pull Substituents and 1,3-Conjugation: A Combined ^{13}C NMR and Computational Study[†]

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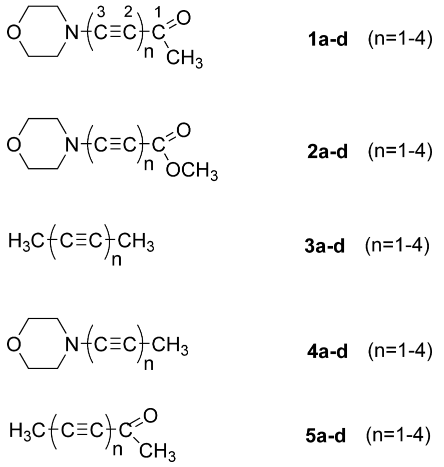
^{13}C chemical shifts of the push−pull oligoalkynes Don-$(C\equiv C)_n$-Acc ($n = 1-4$; Don = morpholino; Acc = COMe, COOMe) were computed at the DFT (B3LYP/6-311+G(d,p) level of theory compared with the experimental δ values and the agreement employed as a measure of quality for the underlying structures. For the global minima structures, 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 various $C\equiv C$ triple bonds were also computed and correlated to each other. The linear dependence obtained for the two parameters $d_{C\equiv C}$ and $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ quantifies changes in π-delocalization induced by the push−pull effect of the substituents and 1,3-conjugation (1,3,5- and 1,3,5,7-, respectively) of the $C\equiv C$ bonds in the oligoalkynes studied. A critical comparison of the push−pull effect, attenuated with increasing n, and the conjugative stabilization of the oligoalkynes, increasing with n, as concluded from $d_{C\equiv C}$ and $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ of the oligoalkynes and the reference compounds Me-$(C\equiv C)_n$-Me, Don-$(C\equiv C)_n$-Me, and Me-$(C\equiv C)_n$-Acc), respectively (Don = morpholino; Acc = COMe, COOMe), is affiliated.

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 $\pi^*_{C=C}/\pi_{C=C}$. (Electron-withdrawing substituents attract π-electron density from the bonding π orbital; electron-releasing substituents donate π-electron density to the antibonding π^* orbital.)[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. [For part i, the push−pull effect must be extremely high to reduce the partial double-bond character sufficiently, for part ii, substitution at $C=C$ must be comparable, and for part iii, exact bond lengths are only available from X-ray studies.]

The occupation quotient $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ can also be successfully applied for the quantification of the push−pull character in substituted alkynes;[6−8] 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 and comparable α-substitution provided. If the latter premises are not ensured, for example, because of differences in steric hindrance[6,7] or ±I in competition with the ±M substituent effects,[8] deviations from the linear dependence $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ versus $d_{C\equiv C}$ were observed and employed to quantify the present electronic situation in terms of bond length and the occupation quotient of the central $C\equiv C$ triple bond. Similar to push−pull alkenes, donor−acceptor-disubstituted alkynes are characterized as push−pull alkynes; the term was introduced by Neuenschwander and Stämpfli.[9]

SCHEME 1: Compounds Studied



1a-d (n=1-4)

2a-d (n=1-4)

3a-d (n=1-4)

4a-d (n=1-4)

5a-d (n=1-4)

The same research group studied the push−pull effect (i.e., π-delocalization induced by push−pull substituents) of the oligoalkynes **1** and **2** ($n = 1-4$) (Scheme 1) employing ^{13}C chemical shift differences between the terminal alkyne carbon atoms[10] and ascertained that π-delocalization via two conjugated $C\equiv C$ triple bonds proves to be very attenuated and that via three conjugated $C\equiv C$ triple bonds proves to be almost not noticeable. Because we have learned to handle ^{13}C chemical shift differences with care as a measure of the push−pull effect in push−pull olefins with proximal structural differences,[1,4,6] both the size of the push−pull effect and π-delocalization in oligoalkynes **1** and **2** ($n = 1-4$) were restudied by employing the generally applicable push−pull parameters occupation quotient $\pi^*_{C\equiv C}/\pi_{C\equiv C}$[2,8] and bond length $d_{C\equiv C}$.[2,5] Hereby, not only should the push−pull effect in the oligoalkynes **1** and **2** ($n = 1-4$) be unequivocally quantified, it was also intended to clear up the controversial discussion concerning the conjugation of 1,3-positioned $C\equiv C$ triple bonds.[11−14]

[†] Dedicated to Professor Alan R. Katritzky (University of Florida) on the occasion of his 80th birthday.

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TABLE 1: Experimental and Computed ^{13}C Chemical Shifts δ(^{13}C)/ppm of the Carbon Atoms in the Oligoalkynes 1−5

compd	C9	C8	C7	C6	C5	C4	C3	C2	C1	$N(CH_2)_2$	$O(CH_2)_2$	CH_3	OCH_3
1a (exptl)							104.5	74.7	182.5	51.2	66.0	31.3	
1a (comput)							111.4	81.7	189.5	55.4	70.9	33.8	
3a							79.84	79.84	3.75	3.75			
4a							90.00	61.06	3.72	56.77	71.53		
4b							100.1	84.04	195.67	4.24		36.14	
2a (exptl)							97.6	62.3	155.7	50.8	65.9		51.7
2a (comput)							104.2	70.0	163.2	54.8	70.9		54.8
1b (exptl)					95.1	53.1	80.6	83.4	182.4	50.0	65.1	31.4	
1b (comput)					105.5	62.2	89.7	94.0	190.9	55.3	71.0	34.6	
3c					76.82	67.53	67.53	76.82	4.05	4.05			
4b					82.47	54.47	67.58	82.59	5.07	55.28	71.08		
5b					97.67	65.91	82.50	73.05	194.60	4.92		35.99	
2b (exptl)					91.0	52.7	75.7	74.1	154.0	50.7	65.7		52.3
2b (comput)					98.8	61.0	82.3	84.0	162.2	54.9	70.9		55.5
1c (exptl)			87.8	54.8	74.8	66.1	77.6	77.4	182.8	50.6	65.6	32.2	
1c (comput)			97.6	65.2	85.4	77.2	87.0	87.6	191.9	55.1	71.1	35.0	
3c			78.59	68.20	61.43	61.43	68.20	78.59	4.24	4.24			
4c			82.44	58.22	61.56	71.69	68.60	83.47	4.70	54.72	70.88		
5c			90.89	67.54	79.44	57.94	82.44	71.18	194.01	4.77		35.86	
2c (exptl)			86.0	54.4	69.4	65.9	73.4	71.4	153.3	50.3	65.6		52.9
2c (comput)			93.2	63.8	78.9	76.1	80.5	79.0	161.7	54.8	70.9		55,9
1d (comput)	92.9	65.9	77.5	80.3	83.3	72.6	85.0	82.7	192.5	54.9	71.2	35.3	
3d	79.56	68.22	61.83	62.04	62.04	61.83	68.22	79.56	4.29	4.29			
4d	82.72	60.64	62.05	74.91	62.13	70.12	68.40	83.83	4.73	54.52	70.81		
5d	87.71	67.77	72.58	60.31	79.76	57.38	82.00	70.20	193.86	4.68		35.78	
2d (exptl)	84.1	55.1	68.2	62.7	67.2	67.4	72.2	70.4	153.1	50.1	65.7		53.5
2d (comput)	89.8	65.1	73.2	79.5	77.5	72.4	78.8	75.8	161.5	54.8	71.0		56.2

The push−pull oligoalkynes **1**−**2** together with reference compounds **3**−**5**, given in Scheme 1, were studied; the structures were computed at the DFT level of theory [B3LYP/6-311+G(d,p)], ^{13}C chemical shifts were computed at the same level using the GIAO method, and the occupation numbers of relevant orbitals were computed by applying an accompanying NBO analysis.[15] Experimental[10] and computed ^{13}C chemical shifts of the carbon atoms, the bond length, and the occupation numbers of bonding π and antibonding π^* orbitals of the C≡C triple bonds in **1**−**5** are given in Tables 1 and 2.

2. Results and Discussion

2.1. ^{13}C Chemical Shifts of Push−Pull Oligoalkynes. The experimental ^{13}C chemical shifts of **1** and **2**, published previously,[10] were correlated with the computed δ values (cf. Figure 1); excellent agreement [$\delta(C{\equiv}C)_{comput} = 1.0243\delta(C{\equiv}C)_{exptl} + 5.18$ ($R^2 = 0.995$)] was obtained. In Figure 2, diagrams are given in which experimental and computed chemical shifts of the carbon atoms of **1c**, **2c**, and **2d** are compared with each other; whereas diagrams for **1c** and **2c** (congruent diagrams can be drawn for **1a,b,d** and **2a,b**, respectively) prove the correct assignment of ^{13}C chemical shifts; δ(^{13}C) values of C6 and C7 in **2d** should be reversed (the assignment procedure[10] was very delicate: ^{13}C labeling of the carbonyl carbons C1 enabled the unequivocal assignment of **1a**−**c** and **2a**−**c** via ^{13}C,^{13}C coupling constants but necessarily had to omit C6 to C9 in **2d**).

The excellent agreement of experimental and computed ^{13}C chemical shifts of the already experimentally studied oligoalkynes **1**−**2**[10] was synchronously strong evidence of accurately computed geometries and electron distribution of the compounds studied. Therefore, for reference purposes (vide infra), we computed the corresponding dimethyl (**3**) and only donor- (**4**) and only acceptor-substituted analogues (**5**) by employing the same procedure.[15] Only the computed ^{13}C chemical shifts δ/ppm of the alkyne carbon atoms and bond lengths of the C≡C triple bonds were employed in the subsequent study.

Neuenschwander and Bartlome[10] compared $\Delta\delta_{C(2){\equiv}C(3)}$ (in **1a**, **2a**), $\Delta\delta_{C(2),C(5)}$ (in **1b**, **2b**), and so on, with respect to π-delocalization induced by the push−pull substituents and concluded a dramatic decrease with an increasing number of conjugated C≡C triple bonds. If $\Delta\delta_{C{\equiv}C}$ however, is correlated with a reliable push−pull parameter, for example, the corresponding bond lengths (to compare only individual C≡C triple bonds is appropriate), then no correlation at all was obtained. This was expected and found for push−pull alkenes[1,2,4,6] and push−pull alkynes[7,8] as well. The ^{13}C chemical shift proves to be dependent on a number of effects,[22] the π-delocalization induced by push−pull substituents being one of them.

This result proves ^{13}C chemical shift differences of alkyne carbon atoms of the C≡C triple bonds to be not qualified as a useful indication of the push−pull character in oligoalkynes.

2.2. Occupation Quotients $\pi^*_{C{\equiv}C}/\pi_{C{\equiv}C}$ and the Push−Pull Effect in Oligoalkynes. Therefore, only the occupation quotient as a push−pull parameter ($\pi^*_{C{\equiv}C}/\pi_{C{\equiv}C}$) remains to be studied with respect to the C≡C triple bond length $d_{C{\equiv}C}$, and it is hereby subjected to the push−pull character in the oligoalkynes **1** and **2**. In Figure 3, 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 $[\pi^*_{C{\equiv}C}(1)/\pi_{C{\equiv}C}(1) + \pi^*_{C{\equiv}C}(2)/\pi_{C{\equiv}C}(2)]$, respectively, versus $d_{C{\equiv}C}$ for **1**−**2** are given. At first glance, the three correlations are not encouraging, but at the second glance, they make sense.

Contrary to push−pull alkenes, in substituted alkynes, two antibonding π^* and two bonding π orbitals of each C≡C triple bond are available for π-delocalization from/to attached substituents, which is dependent on their ±M substituent effects. Therefore, 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 bonds have to be considered and proven to be crucial for the degree of π-delocalization in the compounds studied. In this regard, the donor and acceptor substituents behave differently: whereas the morpholino nitrogen lone pair can be in

TABLE 2: Occupation Numbers of Bonding π and Antibonding π^* Orbitals, Quotients π^*/π, Sum of These Quotients, and Corresponding Bond Lengths of C≡C Triple Bonds in Oligoalkynes 1−5

	occupation of orbitals							bond lengths $d_{C\equiv C}$/Å
compd	$\pi2$ 2−3	$\pi2^*$ 2−3	$\pi1$ 2−3	$\pi1^*$ 2−3	$\pi1^*/\pi1$	$\pi2^*/\pi2$	$\Sigma(\pi1^*/\pi1) + (\pi2^*/\pi2)$	C2−C3
1a	1.8360	0.2384	0.2384	0.0475	0.0243	0.1298	0.154103	1.221
2a	1.8609	0.2343	0.2343	0.0482	0.0246	0.1259	0.150549	1.217
1b	1.8347	0.2015	0.2015	0.0852	0.0449	0.1098	0.154683	1.224
2b	1.8554	0.1938	0.1938	0.0885	0.0466	0.1045	0.151004	1.220
1c	1.8327	0.1799	0.1799	0.0952	0.0504	0.0982	0.148590	1.223
2c	1.8510	0.1724	0.1724	0.0993	0.0525	0.0931	0.145670	1.220
1d	1.8318	0.1652	0.1652	0.0989	0.0525	0.0902	0.142657	1.222
2d	1.8483	0.1590	0.1590	0.1035	0.0548	0.0860	0.140868	1.219
3a	1.9643	0.0650	0.0650	0.0650	0.0331	0.0331	0.066211	1.206
3b	1.9167	0.1026	0.1026	0.1026	0.0535	0.0535	0.107010	1.212
3c	1.8984	0.1096	0.1096	0.1096	0.0577	0.0577	0.115412	1.214
3d	1.8896	0.1112	0.1112	0.1112	0.0588	0.0588	0.117644	1.222
4a	1.9635	0.0570	0.0570	0.1539	0.0782	0.0290	0.107221	1.209
5a	1.8838	0.0624	0.0624	0.0536	0.0273	0.0331	0.060398	1.208
4b	1.9064	0.0952	0.0952	0.1385	0.0718	0.0499	0.121673	1.214
5b	1.8504	0.1148	0.1148	0.0917	0.0478	0.0620	0.109841	1.215
4c	1.8915	0.1050	0.1050	0.1296	0.0678	0.0555	0.123311	1.215
5c	1.8396	0.1260	0.1260	0.0985	0.0518	0.0685	0.120322	1.217
4d	1.8856	0.1089	0.1089	0.1239	0.0652	0.0578	0.122973	1.216
5d	1.8351	0.1292	0.1292	0.1001	0.0528	0.0704	0.123250	1.218
	$\pi2$ 4−5	$\pi2^*$ 4−5	$\pi1$ 4−5	$\pi1^*$ 4−5	$\pi1^*/\pi1$	$\pi2^*/\pi2$	$(\pi1^*/\pi1) + (\pi2^*/\pi2)$	C4−C5
1b	1.8192	0.2653	1.9117	0.1090	0.0570	0.1458	0.202851	1.225
2b	1.8320	0.2589	1.9096	0.1044	0.0547	0.1413	0.195992	1.224
1c	1.8162	0.2345	1.8497	0.1551	0.0839	0.1291	0.212967	1.230
2c	1.8261	0.2287	1.8491	0.1516	0.0820	0.1252	0.207225	1.228
1d	1.8129	0.2172	1.8357	0.1686	0.0918	0.1198	0.211653	1.230
2d	1.8209	0.2128	1.8354	0.1658	0.0903	0.1169	0.207200	1.229
3b	1.9167	0.1026	1.9167	0.1026	0.0535	0.0535	0.107010	1.212
3c	1.8701	0.1555	1.8701	0.1555	0.0831	0.0831	0.166258	1.220
3d	1.8517	0.1680	1.8517	0.1680	0.0908	0.0908	0.181502	1.228
4b	1.9027	0.2177	1.9201	0.1019	0.0530	0.1144	0.167452	1.218
5b	1.8776	0.0931	1.9116	0.1026	0.0537	0.0496	0.103283	1.212
4c	1.8596	0.1499	1.8749	0.2025	0.1080	0.0806	0.188614	1.224
5c	1.8365	0.1566	1.8660	0.1518	0.0813	0.0853	0.166591	1.221
4d	1.8438	0.1644	1.8595	0.1942	0.1045	0.0891	0.193610	1.226
5d	1.8219	0.1666	1.8486	0.1695	0.0917	0.0914	0.183123	1.224
	$\pi2$ 6−7	$\pi2^*$ 6−7	$\pi1$ 6−7	$\pi1^*$ 6−7	$\pi1^*/\pi1$	$\pi2^*/\pi2$	$(\pi1^*/\pi1) + (\pi2^*/\pi2)$	C6−C7
1c	1.8100	0.2728	1.8970	0.182	0.0623	0.1507	0.213027	1.228
2c	1.8190	0.2676	1.8960	0.1151	0.0607	0.1471	0.207821	1.226
1d	1.8080	0.2444	1.8325	0.1682	0.0918	0.1352	0.226964	1.232
2d	1.8141	0.2414	1.8321	0.1659	0.0906	0.1331	0.223621	1.232
3c	1.8984	0.1096	1.8984	0.1096	0.0577	0.0577	0.115412	1.214
3d	1.8517	0.1680	1.8517	0.1680	0.0908	0.0908	0.181502	1.228
4c	1.8683	0.2408	1.9037	0.1125	0.0591	0.1289	0.187944	1.222
5c	1.8757	0.1091	1.8936	0.1023	0.0540	0.0582	0.112227	1.214
4d	1.8407	0.1642	1.8484	0.2234	0.1208	0.0892	0.210029	1.229
5d	1.8316	0.1637	1.8477	0.1686	0.0913	0.0894	0.180625	1.224
	$\pi2$ 8−9	$\pi2^*$ 8−9	$\pi1$ 8−9	$\pi1^*$ 8−9	$\pi1^*/\pi1$	$\pi2^*/\pi2$	$(\pi1^*/\pi1) + (\pi2^*/\pi2)$	C8−C9
1d	1.8054	0.2760	1.8905	0.1209	0.0640	0.1529	0.216826	1.228
2d	1.8111	0.2733	1.8899	0.1190	0.0630	0.1509	0.213869	1.228
3d	1.8896	0.1112	1.8896	0.1112	0.0588	0.0588	0.117644	1.222
4d	1.8476	0.2532	1.8958	0.1166	0.0615	0.1370	0.198570	1.224
5d	1.8747	0.1061	1.8851	0.1105	0.0586	0.0566	0.115181	1.215

conjugation with the $\pi(2)$ orbital only (perpendicular to the $R_2N-C\equiv$ plane), the acceptor substituents can be in conjugation with both $\pi(2)$ (by conjugation with the π orbital of the C=O double bond) and $\pi(1)$ (by conjugation with the π-like orbital of one of the oxygen lone pairs of the C=O group). Therefore, separated dependences in the correlations $\pi^*(1)/\pi(1)$ versus $d_{C\equiv C}$ and $\pi^*(2)/\pi(2)$ versus $d_{C\equiv C}$ have been obtained (cf. Figure 3a,b) subject to the C≡C triple bond studied; if the sum of the quotients is correlated $[(\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)]$ versus $d_{C\equiv C}$; cf. Figure 3c), then the complete push−pull π conjugation is dealt with and the expected dependence is obtained, which proves the occupation quotient $[(\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)]$, as well as the partial bond length $d_{C\equiv C}$, to be a reliable indication to quantify the push−pull effect in these compounds.

The search for X-ray structures of oligoalkynes in the Cambridge Structural Database[23] yielded, among others given in Table 3, data for only **1b**, **2b**, and **3c**; the comparison of

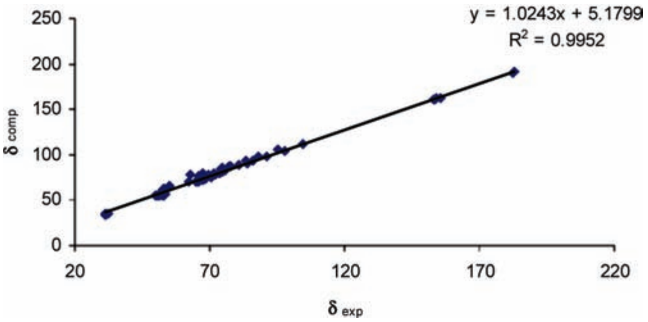


Figure 1. Linear dependence of experimental and computed ^{13}C chemical shifts δ/ppm of oligoalkynes **1** and **2**.

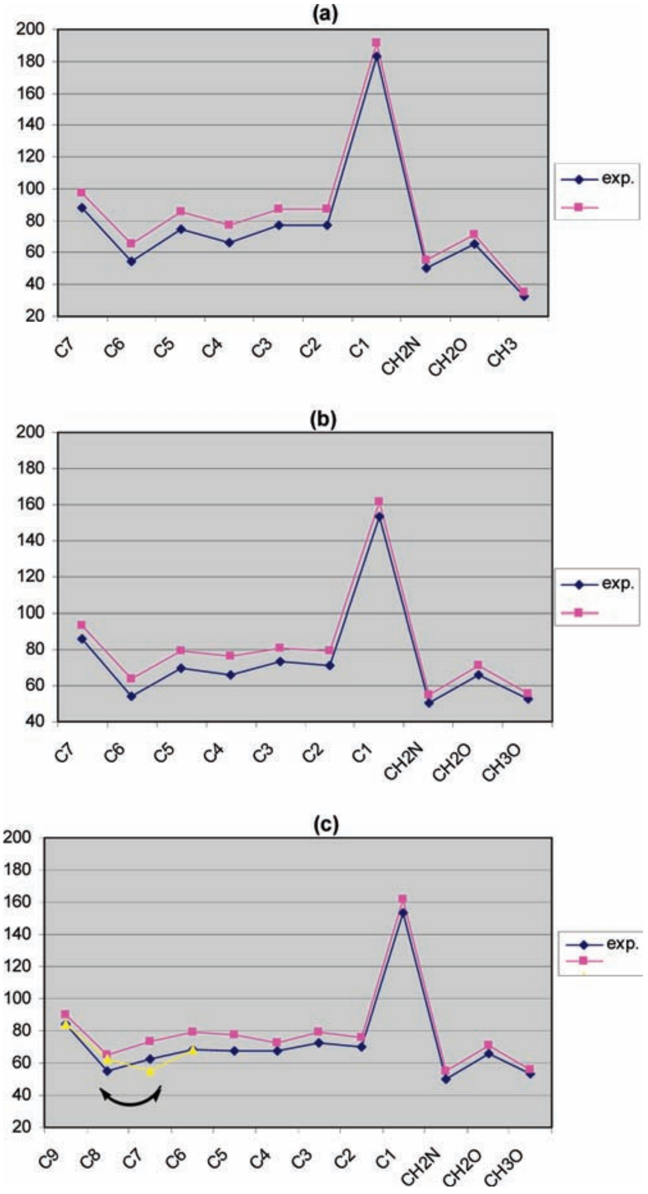


Figure 2. Diagrams for comparison of computed and experimental ^{13}C chemical shifts of oligoalkynes (a) **1c**, (b) **2c**, and (c) **2d**.

these experimental data with the computed ones, calculated in solution and not considering packing forces, yielded generally longer computed bond lengths. The relative size, however, is correctly reproduced. Experimental changes in C≡C triple bond lengths of **1b**, **2b**, and **3c** are $\Delta d_{C\equiv C} = 0.017$ Å only, in acceptable agreement with the computed values ($\Delta d_{C\equiv C} = 0.014$ Å).

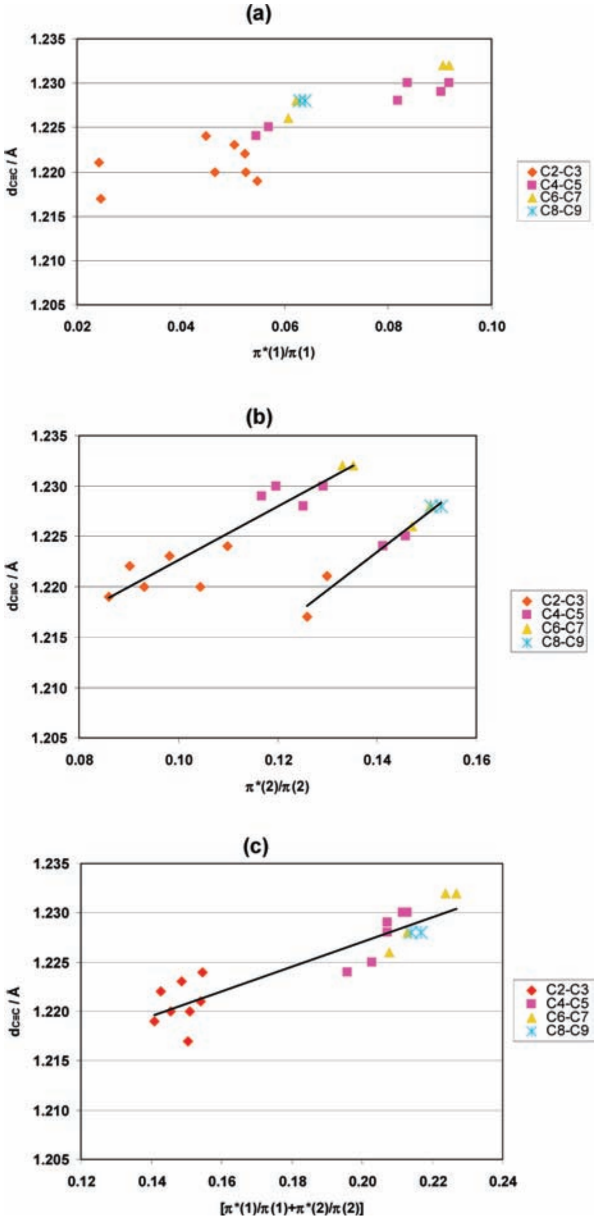
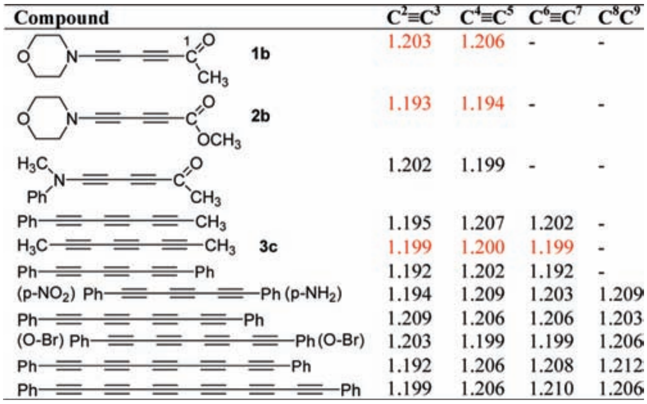


Figure 3. Correlations of the quotients (a) $\pi^*(1)/\pi(1)$, (b) $\pi^*(2)/\pi(2)$, and (c) $[\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)]$, respectively, to the bond lengths $d_{C\equiv C}$/Å in the oligoalkynes **1** and **2**.

TABLE 3: X-ray Bond Lengths in Oligoalkynes 1−5 ($d_{C\equiv C}$/Å Published in CSD)[23]



Compound	$C^2\equiv C^3$	$C^4\equiv C^5$	$C^6\equiv C^7$	C^8C^9
1b	1.203	1.206	-	-
2b	1.193	1.194	-	-
$H_3C(Ph)N-C\equiv C-C\equiv C-C(=O)CH_3$	1.202	1.199	-	-
$Ph-C\equiv C-C\equiv C-C\equiv C-CH_3$	1.195	1.207	1.202	-
$H_3C-C\equiv C-C\equiv C-C\equiv C-CH_3$ **3c**	1.199	1.200	1.199	-
$Ph-C\equiv C-C\equiv C-C\equiv C-Ph$	1.192	1.202	1.192	-
(p-NO$_2$) $Ph-C\equiv C-C\equiv C-C\equiv C-Ph$ (p-NH$_2$)	1.194	1.209	1.203	1.209
$Ph-C\equiv C-C\equiv C-C\equiv C-C\equiv C-Ph$	1.209	1.206	1.206	1.203
(O-Br) $Ph-C\equiv C-C\equiv C-C\equiv C-C\equiv C-Ph$ (O-Br)	1.203	1.199	1.199	1.206
$Ph-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-Ph$	1.192	1.206	1.208	1.212
$Ph-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-C\equiv C-Ph$	1.199	1.206	1.210	1.206

2.3. Push−Pull Effect and π Conjugation in Oligoalkynes.

In addition to the push−pull oligoalkynes **1**−**2**, which are experimentally available,[10] the dimethyl analogues **3** (for

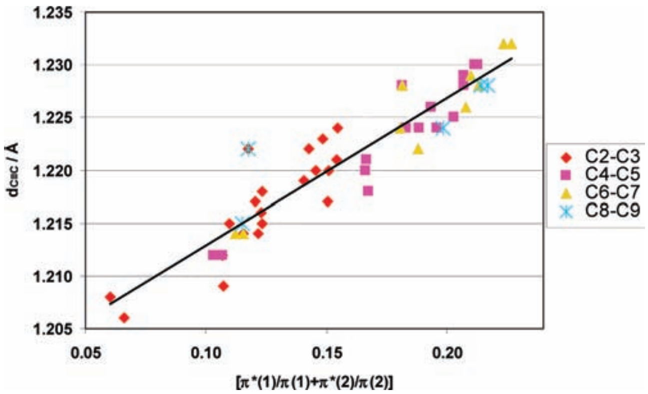
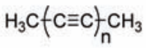
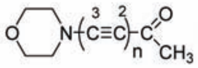


Figure 4. Correlation of the quotients [$\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] to the bond lengths $d_{C\equiv C}$/Å in the oligoalkynes **1**−**5**.

TABLE 4: Occupation Quotients [$\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] of Oligoalkynes 3 (Red) and 1 and Differences between the Two Groups of Compounds Δ(quotients) (Blue)

Compound	n=1	n=2	n=3	n=4
 $H_3C\text{-}(C\equiv C)_n\text{-}CH_3$	0.066	0.107	0.1155	0.118
	0.154	0.155	0.1486	0.1427
$C^5\equiv C^4$	-	0.107	0.1166	0.1815
	-	0.203	0.213	0.212
$C^7\equiv C^6$	-	-	0.1155	0.1815
	-	-	0.213	0.227
$C^9\equiv C^8$	-	-	-	0.118
	-	-	-	0.217
Δ(quotients) $C^2\equiv C^3$	0.088	0.048	0.034	0.025
Δ(quotients) $C^4\equiv C^5$	-	0.096	0.047	0.031
Δ(quotients) $C^6\equiv C^7$	-	-	0.098	0.046
Δ(quotients) $C^8\equiv C^9$	-	-	-	0.099

studying π conjugation of the C≡C triple bonds only) and the donor (**4**) and the acceptor analogues **5** (for studying π conjugation subject to donor and acceptor substitution, respectively) were computed by employing the same procedure.[15] The results are involved in Tables 1 and 2. The corresponding push−pull parameters of **3**−**5** were included into the [($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] versus $d_{C\equiv C}$ correlation, given in Figure 4. All values of **1**−**5** fit in the correlation and prove π-delocalization in oligoalkynes (induced or not induced by push−pull substituents) to be dominated by C≡C triple bond/C≡C triple bond, C≡C triple bond/substituent conjugation, or both.

But how do we separate the two effects? Both elongate the bond length of the C≡C triple bonds and increase the occupation quotient. Therefore, first, the methyl analogues **3** were studied: (i) Starting from Me−C≡C−Me (**3a**) via 1,3-di-C≡C− (**3b**) and 1,3,5-tris-C≡C− (**3c**) to 1,3,5,7-tetra-C≡C− (**3d**), both bond length and occupation quotient are increasing (in **3c,d**, two pairs of values each), indicating rising π-delocalization in the oligoalkynes **3** with increasing number of conjugated C≡C triple bonds. If the terminal C≡C triple bond is considered only, then the effect is strongest when comparing **3a** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.066) and **3b** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.107) and diminishes to **3c** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.1155) and **3d** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.1175), respectively. In the latter two cases, however, there are additionally one or two inner C≡C triple bonds, respectively, and these show the undamped effect of rising π-delocalization with increasing number of 1,3-conjugated C≡C triple bonds (**3c**: [($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.166; **3d**: [($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.1815) (cf. Table 2). (ii) The same effect of increasing π conjugation can be reported for the only donor- (**4**) and only acceptor-substituted oligoalkynes **5**. (iii) However, the largest π-delocalization effects in each row of n = 1 to 4 were obtained for the push−pull oligoalkynes **1** and **2**: **1a** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.154), **1b** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.154 and 0.203, respectively), **1c** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.1485, 0.213, and 0.213, respectively), and **1d** ([($\pi^*(1)/\pi(1) + \pi^*(2)/\pi(2)$] = 0.143, 0.212, 0.227, and 0.217, respectively). Obviously, in addition to π conjugation of the 1,3-positioned C≡C triple bonds, further π-delocalization induced by the push−pull substituents appears to be active, and this is so in all compounds **1** and **2** and in all of their C≡C triple bonds. (iv) The quotient data of **1**−**3** are given in Table 4. The data of oligoalkynes **3** (red) can be compared with respect

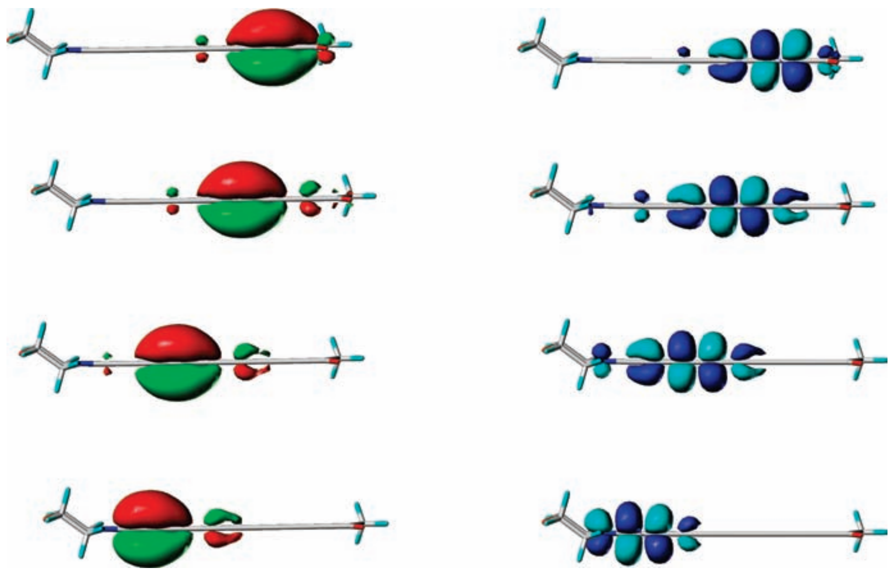


Figure 5. Visualization of both the bonding π orbitals (left) and antibonding π* orbitals (right) of the C≡C triple bonds of push−pull-tetra-alkyne **1d**.

to π-delocalization of the 1,3-conjugated (1,3,5- and 1,3,5,7-) $C\equiv C$ triple bonds only and show that π conjugation increases with more $C\equiv C$ triple bonds in the 1,3-position. The slope is not linear but approaches a limiting value, which, with four 1,3-conjugated $C\equiv C$ triple bonds, is not yet reached, as was the case in 1,3-conjugated $C{=}C$ double bonds.[24] (v) Differences (blue) of quotients of push−pull oligoalkynes **1** and the reference data of **3** can be compared with respect to the additional effect induced by the push−pull substituents on the π-delocalization. These differences (synonymous for the additional push−pull effect) are strongest for $n = 1$ (0.088) and then diminish from $n = 2$ (0.048) and 3 (0.034) to 4 (0.025), which is in complete agreement with the decreasing push−pull effect with increasing numbers of conjugated $C\equiv C$ triple bonds. It should be emphasized, however, that this push−pull effect proves to be still active via π-delocalization over four conjugated $C\equiv C$ triple bond*s*. (vi) This electronic evidence of the presence of considerable push−pull effect even via four 1,3-conjugated $C\equiv C$ triple bonds is also apparent in the bonding $\pi_{C\equiv C}$ and antibonding $\pi^*_{C\equiv C}$ orbitals of the oligoalkynes **1** and **2**. (In Figure 5, for example, the corresponding orbitals for **1d** are given; the same dependences can be found for **1a**−**c** and **2a**−**d**). In general, the bonding π orbitals send more π-electron density into the conjugated π orbital of the adjacent conjugated $C\equiv C$ triple bond at the acceptor side, whereas the antibonding π^* orbital collects more π-electron density into the conjugated antibonding π^* orbital at the donor side of the molecule. These orbital diagrams corroborate with the above-mentioned occupation quotient dependences.

3. Conclusions

Both ^{13}C chemical shift differences $\Delta\delta_{C\equiv C}$ and occupation quotients $\pi^*_{C\equiv C}/\pi_{C\equiv C}$ with respect to the bond lengths $d_{C\equiv C}$ of $C\equiv C$ triple bonds were employed to indicate π-delocalization, induced by both π conjugation of 1,3-$C\equiv C$ triple bonds and push−pull substitution in a number of push−pull oligoalkynes **1** and **2**. Whereas $\Delta\delta_{C\equiv C}$ values proved to be useless in this context, the occupation quotients represent a complete picture of this phenomenon. π-Delocalization of conjugated $C\equiv C$ triple bonds increases with more $C\equiv C$ triple bonds in the 1,3-position. The slope is not linear but approaches a limiting value, which, with four conjugated $C\equiv C$ triple bonds, is not yet reached. π-Delocalization induced by the push−pull substituents (the push−pull effect) in the oligoalkynes Don$(\text{-}C\equiv C-)_n$Acc is strongest for $n = 1$ and diminishes from $n = 2$ to 4 in complete agreement with the decreasing push−pull effect with growing numbers of conjugated $C\equiv C$ triple bonds. It should be emphasized, however, that the push−pull effect proves to be still active via π-delocalization over four conjugated $C\equiv C$ triple bonds.

Supporting Information Available: Absolute energies and Cartesian coordinates computed at the B3LYP/6-311+G(d,p) level of theory (including solvent model SCRF) for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Quantum chemical calculations were performed on workstations using the Gaussian 03 software package.[16] DFT calculations were performed at the B3LYP/6-311+G(d,p) level of theory. The population of the orbitals and lone pairs of **1** and **2** were calculated by NBO analysis[17] and refer to the B3LYP/6-311+G(d,p) molecular geometries. Chemical shieldings were calculated at the same level of theory using the GIAO method[18,19] and referenced to TMS shielding values, also calculated at the same level of theory, to obtain chemical shifts. In all computations, the solvent $CDCl_3$ (dielectricity constant 4.81) was considered employing the SCRF-IEF PCM model.[20] The NBO 5.0 population analysis[17] was used linked to the Gaussian 03 program package.[16] Resulting nonlinear molecular orbitals (NLMOs) from this NBO module were graphically illustrated using the program SYBYL.[21]

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