Quantification of the Push−Pull Character of Donor−Acceptor Triazenes

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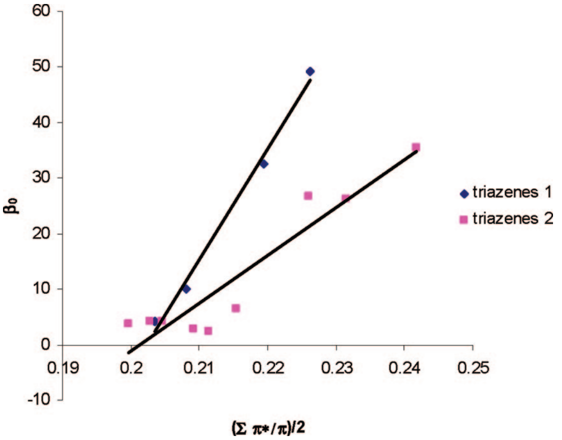
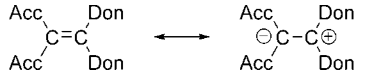


The push−pull character of two series of donor−acceptor triazenes has been quantified by ^{13}C and ^{15}N chemical shift differences of the partial N(1)=N(2) and N(3)=C(4) double bonds in the central linking C=N−N=N−C unit and by the quotient of the occupations of both the bonding π and antibonding orbitals π^* of these partial double bonds. Excellent correlations of the two estimates, to quantify the push−pull effect, with the bond lengths strongly recommend the occupation quotients π^*/π, the ^{15}N chemical shift differences $\Delta\delta$[N(1),N(2)], and the corresponding bond lengths as reasonable sensors for quantifying *charge alternation* along the C=N−N=N−C linking unit, for the donor−acceptor quality of the triazenes **1** and **2** and for the molecular hyperpolarizability β_0 of these compounds. Within this context, certain substances can be strongly recommended for NLO application.

Introduction

Bond polarization of donor−acceptor substituted double bonds and conjugated larger chromophores can be readily studied by the corresponding bond lengths or the ^{13}C chemical shift differences $\Delta\delta(^{13}C)$: the corresponding *push−pull effect* causes charge polarization (cf. Scheme 1), which increases both the bond length and $\Delta\delta(^{13}C)$.[1]

SCHEME 1



Besides these two parameters to quantify the donor−acceptor character, alternatively, the restricted rotation about the partial C=C double bond[2,3] (which can be studied on the NMR time scale if the corresponding barrier $\Delta G^\ddagger$ proves to be lower than 22−23 kcal/mol) and the occupation quotient π^*/π of the partial C=C double bond (electron-releasing substituents donate π-electron density into $\pi^*_{C=C}$, electron-withdrawing substituents attract π-electron density from $\pi_{C=C}$, both elongating the corresponding

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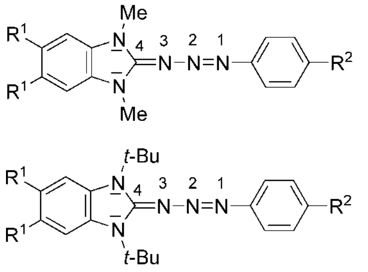
SCHEME 2



	R^1	R^2
1a	H	H
1b	H	NO_2
1c	OMe	H
1d	OMe	NO_2

	R^1	R^2
2a	H	H
2b	OMe	H
2c	F	H
2d	H	OMe
2e	H	NO_2
2f	F	OMe
2g	F	NO_2
2h	OMe	OMe
2i	OMe	NO_2

partial double bond) can be employed.[4,5] While the application of the bond lengths is restricted to solid state measurements (X-ray diffraction), the barrier to rotation is limited to a window of 10–23 kcal/mol[4a,5] and employing $\Delta\delta(^{13}C)$ is restricted to identical α,β-substitution patterns of the partial C=C double bond,[4] the occupation quotient π^*/π of the partial C=C double bond proves to be a reliable and generally applicable parameter to quantify the push–pull effect in this kind of compound.[5]

Because donor–acceptor substituted double bonds (push–pull alkenes) and conjugated larger chromophores, in addition, exhibit large molecular dipoles, often extremely high molecular hyperpolarizabilities, β,[6–10] and strong intramolecular charge transfer bands, [11] these kinds of compounds are most promising materials for NLO applications.[8] Appropriate correlations of $\pi^*_{C=C}/\pi_{C=C}$ and β_0 corroborate the occupation quotient to be not only a useful indicator of the push–pull effect but also of the inherent molecular hyperpolarizability β_0 of the donor–acceptor substituted chromophores of interest.[1]

It is the aim of this paper to extend our studies to two series of donor–acceptor triazenes **1** and **2** (cf. Scheme 2), published recently by Khramov and Bielawski,[12] and this for two reasons: (i) Can ^{15}N chemical shift differences $\Delta\delta(^{15}N)$ in **1** and **2** be employed similarly to $\Delta\delta(^{13}C)$ in push–pull alkenes to quantify the donor–acceptor character[4,5] of these compounds? (ii) About the diazo bridge both the activity as conjugation stopper[13,14] and structural trends consistent with delocalization within the azine framework[15,16] were reported. In order to study both (i) and (ii) in the case of triazenes, ^{15}N chemical shifts, occupation quotients π^*/π, and molecular hyperpolarizabilities β_0 of **1** and **2** were calculated and employed to quantify the donor–acceptor properties of the latter compounds[12] and their potential application as NLO materials.

Computational Details

Ab Initio MO Calculations and the Natural Bond Orbital (NBO) Population Analysis[17] were performed using *Gaussian03,*[18] geometry optimizations at the B3LYP/6–311G** level of theory without constraints.[19] The molecules **1** and **2** (see Scheme 2) are not completely flat but twisted up to 30°; appropriate dihedral angles are given in Table 1. The occupation of antibonding π^*, bonding orbitals π, the quotient π^*/π and the corresponding bond lengths d/Å of the partial N=N and C=N double bonds in the linking chain C=N–N=N–C are given in Table 2. Molecular hyperpolarizabilities at zero frequency β_0 were calculated using the same model chemistry and the default parameters provided by the "*polar=enonly*" *Gaussian03* key word and are included into Table 2. Both the size of the basis set and the inclusion of diffuse functions were found to be of negligible influence on the quality of the correlations.

^{15}N and ^{13}C NMR chemical shifts were calculated by using the GIAO method[20] at the B3LYP/6-311G** level of theory (reference compounds TMS and nitromethane were calculated at the same level); a solvent was not considered. The $^{15}N/^{13}C$ chemical shifts and chemical shift differences $\Delta\delta(^{15}N,^{15}N)/\Delta\delta(^{15}N,^{13}C)$ together with the corresponding bond lengths d are given in Table 3.

All calculations were carried out on SGI workstations and LINUX clusters.

Results and Discussion

Steric Hindrance in Triazenes 1 and 2. The triazenes studied are not completely flat but slightly twisted. This steric hindrance is almost negligible in the linking chain C(4)=N(3)–N(2)=N(1)–C (<8°, cf. Table 1) but increases in the terminal parts of the molecules. It is approximately 20° [N(2)–N(1)–C(*i*)–C(*o*)] in the N(1)-phenyl moiety of both **1** and **2**, and at the donor sides of the molecules, it is about 10° in the *N*-methyl triazenes **1** and about 30° in the corresponding *N*-*tert*-butyl analogs **2** [N(2)–N(3)–C(4)–N, cf. Table 1]. Similar conclusions can be drawn by comparing the dihedral angles between either the donor or acceptor components and the triazeno linkage; see Table 1. In light of these data, the delocalization along the donor–acceptor triazenes studied is somewhat hindered and more so in the *tert*-butyl compounds **2** than in their *N*-methyl analogs **1**. Thus, from this structural point of view, the π-electron delocalization along the donor–acceptor substituted chromophore in **2** should be somewhat reduced compared with the *N*-methyl analogs **1**. It will be exciting to learn whether these structural influences are indicated by the suggested parameters for quantifying the push–pull effect in these molecules (vide infra).[21]

Bond Length and Occupation Coefficient for Quantifying the Push–Pull Effect in Triazenes 1 and 2. Both push–pull parameters bond lengths d and occupation quotients

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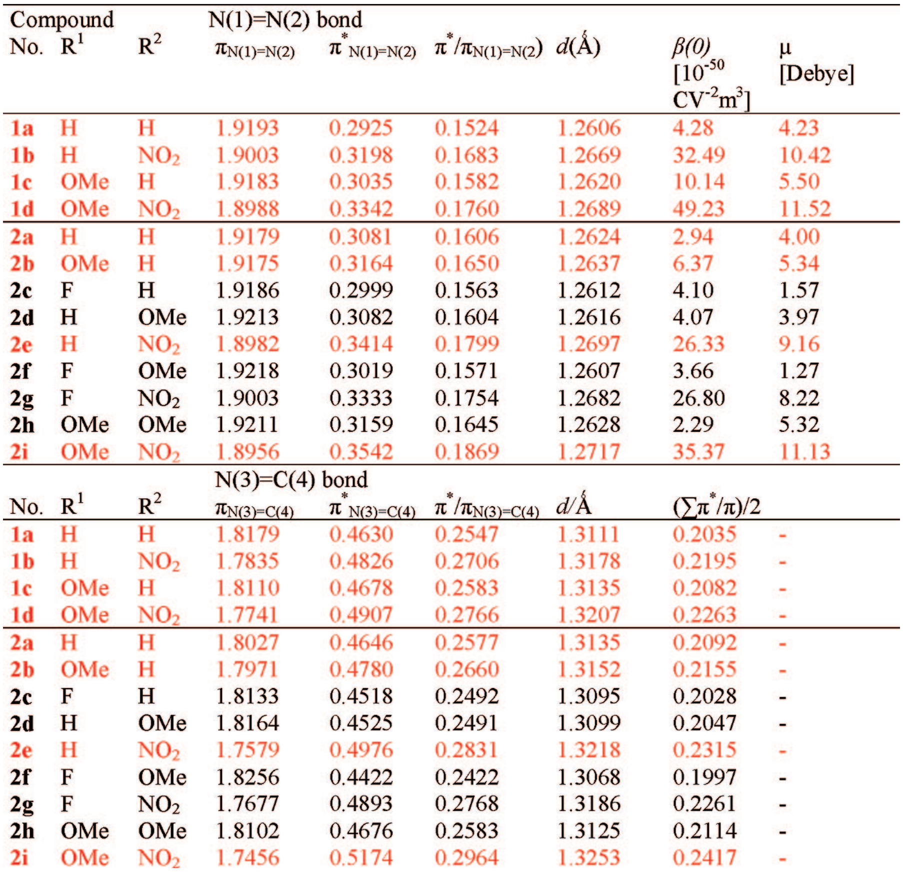
TABLE 1. Certain Dihedral Angles of Molecules 1 and 2

compound			dihedral angles				angles between planes	
No.	R^1	R^2	N−C(4)−N(3)−N(2)	C(4)−N(3)−N(2)−N(1)	N(3)−N(2)−N(1)−C(*i*)	N(2)−N(1)−C(*i*)−C(*o*)	N−C(4)−N//(1)−N(2)−N(3)	C(*o*)−C(*i*)− C(*o*′)//N(1)−N(2)−N(3)
1a	H	H	171.3	172.2	176.2	160.6	14.9	22.5
1b	H	NO_2	169.7	173.0	175.9	162.8	15.8	20.6
1c	OMe	H	169.1	172.9	175.6	161.7	14.1	21.7
1d	OMe	NO_2	169.2	172.9	175.6	161.7	16.5	21.9
2a	H	H	149.7	173.2	173.0	159.9	31.9	25.4
2b	OMe	H	149.2	172.3	173.1	159.4	33.2	25.9
2c	F	H	151.5	172.9	173.2	160.5	30.3	24.7
2d	H	OMe	150.9	172.6	172.6	162.0	30.9	23.9
2e	H	NO_2	146.2	174.3	172.7	161.4	35.0	24.2
2f	F	OMe	152.1	172.1	173.0	162.0	28.9	23.5
2g	F	NO_2	146.6	174.5	172.7	161.7	34.6	24.3
2h	OMe	OMe	150.0	172.0	172.8	161.3	32.4	24.2
2i	OMe	NO_2	144.1	174.8	172.8	161.7	37.0	23.8

TABLE 2. Occupation Numbers of Antibonding π^* and Bonding π Orbitals and Bond Lengths of the Corresponding Partial N(1)═N(2) and N(3)═C(4) Double Bonds, Molecular Hyperpolarizabilities at Zero Frequencies, β_0, and Dipole Moments, μ, of Triazenes 1 and 2



Compound			N(1)=N(2) bond					
No.	R^1	R^2	$\pi_{N(1)=N(2)}$	$\pi^*_{N(1)=N(2)}$	$\pi^*/\pi_{N(1)=N(2)}$	*d*(Å)	*β(0)* [10^{-50} $CV^{-2}m^3$]	μ [Debye]
1a	H	H	1.9193	0.2925	0.1524	1.2606	4.28	4.23
1b	H	NO_2	1.9003	0.3198	0.1683	1.2669	32.49	10.42
1c	OMe	H	1.9183	0.3035	0.1582	1.2620	10.14	5.50
1d	OMe	NO_2	1.8988	0.3342	0.1760	1.2689	49.23	11.52
2a	H	H	1.9179	0.3081	0.1606	1.2624	2.94	4.00
2b	OMe	H	1.9175	0.3164	0.1650	1.2637	6.37	5.34
2c	F	H	1.9186	0.2999	0.1563	1.2612	4.10	1.57
2d	H	OMe	1.9213	0.3082	0.1604	1.2616	4.07	3.97
2e	H	NO_2	1.8982	0.3414	0.1799	1.2697	26.33	9.16
2f	F	OMe	1.9218	0.3019	0.1571	1.2607	3.66	1.27
2g	F	NO_2	1.9003	0.3333	0.1754	1.2682	26.80	8.22
2h	OMe	OMe	1.9211	0.3159	0.1645	1.2628	2.29	5.32
2i	OMe	NO_2	1.8956	0.3542	0.1869	1.2717	35.37	11.13

			N(3)=C(4) bond					
No.	R^1	R^2	$\pi_{N(3)=C(4)}$	$\pi^*_{N(3)=C(4)}$	$\pi^*/\pi_{N(3)=C(4)}$	*d*/Å	$(\sum\pi^*/\pi)/2$	
1a	H	H	1.8179	0.4630	0.2547	1.3111	0.2035	-
1b	H	NO_2	1.7835	0.4826	0.2706	1.3178	0.2195	-
1c	OMe	H	1.8110	0.4678	0.2583	1.3135	0.2082	-
1d	OMe	NO_2	1.7741	0.4907	0.2766	1.3207	0.2263	-
2a	H	H	1.8027	0.4646	0.2577	1.3135	0.2092	-
2b	OMe	H	1.7971	0.4780	0.2660	1.3152	0.2155	-
2c	F	H	1.8133	0.4518	0.2492	1.3095	0.2028	-
2d	H	OMe	1.8164	0.4525	0.2491	1.3099	0.2047	-
2e	H	NO_2	1.7579	0.4976	0.2831	1.3218	0.2315	-
2f	F	OMe	1.8256	0.4422	0.2422	1.3068	0.1997	-
2g	F	NO_2	1.7677	0.4893	0.2768	1.3186	0.2261	-
2h	OMe	OMe	1.8102	0.4676	0.2583	1.3125	0.2114	-
2i	OMe	NO_2	1.7456	0.5174	0.2964	1.3253	0.2417	-

π^*/π of the partial N(1)═N(2) and N(3)═C(4) double bonds in the donor−acceptor linking chain C(4)═N(3)−N(2)═N(1)−C(*i*) were considered; data are given in Table 2 and the corresponding values are correlated in Figures 1 and 2. The correlations are excellent and point in the correct direction: with increasing donor−acceptor character of the triazenes **1** and **2** (cf. **4** in Scheme 3), the two partial double bonds are elongated; thereby the occupation quotients $\pi^*_{N(1)=N(2)}/\pi_{N(1)=N(2)}$ and $\pi^*_{N(3)=C(4)}/\pi_{N(3)=C(4)}$ are changed because of changes in π-bond orders (see data in Table 2). The same conclusions with respect to the donor−acceptor character of molecules **1** and **2** can be drawn from the dipole moments of the compounds, additionally included in Table 2.

If comparable values of compounds **1** and **2** are compared (marked in Table 2), the corresponding push−pull effect proves to be larger in the *N*-*t*-Bu compounds **2** than in the *N*-Me analogs **1**; in the light of greater steric strain in **2** (vide supra), obviously, this *N*-alkyl volume effect is more than compensated for by the larger +I effect of the two *tert*-butyl substituents at the nitrogen atoms compared with the corresponding *N*-methyl substituent effects in **1**.

Barriers to rotation about the partial N(1)═N(2) and N(3)═C(4) double bonds are not expected because the occupation quotients π^*/π obtained for the two bonds (cf. Table 2) are far below 0.2, the borderline for having a chance to measure the corresponding barriers to rotation on the NMR time scale.[5]

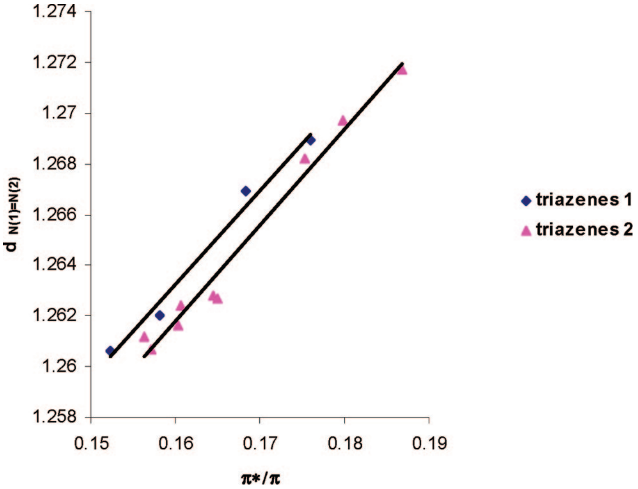


FIGURE 1. Correlation of bond lengths in Å and occupation coefficients $\pi^*_{N(1)=N(2)}/\pi_{N(1)=N(2)}$ of the partial N(1)=N(2) double bond in triazenes **1** ($d_{N(1)=N(2)} = 0.3722\pi^*/\pi + 1.2037$; $R^2 = 0.9834$) and **2** ($d_{N(1)=N(2)} = 0.3776\pi^*/\pi + 1.2014$; $R^2 = 0.9787$).

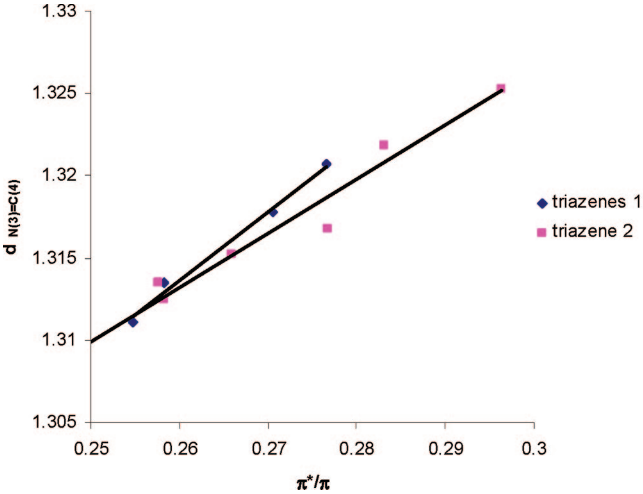


FIGURE 2. Correlation of bond lengths in Å and occupation coefficients $\pi^*_{N(3)=C(4)}/\pi_{N(3)=C(4)}$ of the partial N(3)=C(4) double bond in triazenes **1** ($d_{N(1)=N(2)} = 0.4161\pi^*/\pi + 1.2055$; $R^2 = 0.9907$) and **2** ($d_{N(1)=N(2)} = 0.33\pi^*/\pi + 1.2274$; $R^2 = 0.9781$).

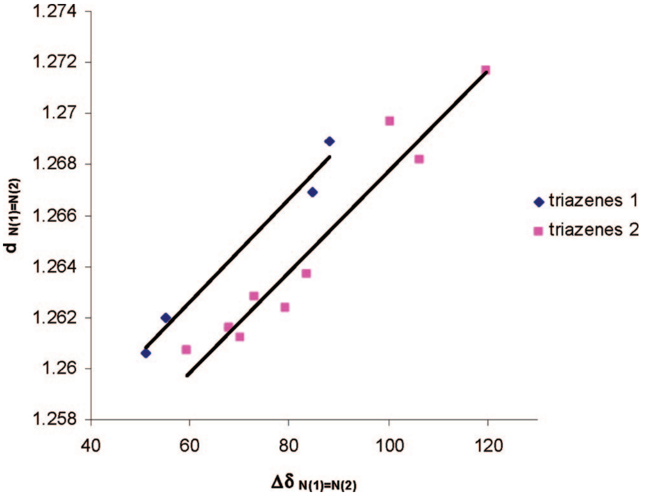
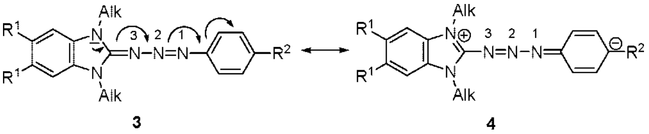


FIGURE 3. Correlation of bond lengths in Å and ^{15}N chemical shift differences $\Delta\delta$[N(1),N(2)] (ppm) of the partial N(1)=N(2) double bond in triazenes **1** ($d_{N(1)=N(2)} = 0.0002\Delta\delta_{N(1)=N(2)} + 1.2505$; $R^2 = 0.9768$) and **2** ($d_{N(1)=N(2)} = 0.0002\Delta\delta_{N(1)=N(2)} + 1.248$; $R^2 = 0.9405$).

SCHEME 3



Summarizing the results obtained so far: the two parameters (bond lengths *d* and occupation quotients π^*/π of partial N=N and N=C double bonds) are unequivocally corroborated to be excellent and generally applicable sensors of the donor−acceptor character of appropriately polarized molecules.

Chemical Shift Differences Δδ for Quantifying the Push−Pull Effect in Triazenes. Alternatively to $\Delta\delta(^{13}C)$ in push−pull olefins,[1,3,4] the chemical shift differences $\Delta\delta$[N(1),N(2)] and $\Delta\delta$[N(3),C(4)] in the triazenes **1** and **2** should be similarly useful sensors of the corresponding push−pull effect. Chemical shifts are given in Table 3 and are correlated in Figures 3 and 4 to the corresponding bond lengths, another reliable push−pull effect indicator (employed already in former correlations as given in Table 2 and Figures 1 and 2).

The $\Delta\delta(^{15}N)$ correlation of the partial N(1)=N(2) double bond, given in Figure 3, proves to be excellent and is pointing in the correct direction: With increasing donor−acceptor character of the triazenes, N(1)=N(2) bond lengths increase, strengthening hereby the polarization of the partial N(1)=N(2) double bond, which is corroborated by increasing ^{15}N chemical shift differences (cf. Figure 3). The same is true for the

TABLE 3. Certain $^{15}N/^{13}C$ Chemical Shifts (δ, ppm) of Triazenes 1 and 2 Calculated at the B3LYP/6-311G Level of Theory**

Compound			$^{15}N/^{13}C$ chemical shifts							
No.	R1	R2	δ (N-1)	δ (N-2)	δ (N-3)	δ (C-4)	Δδ (N-1-N2)	Δδ (N-3-C4)	d/Å(N-1-N-2)	d/Å(N-3-C4)
1a	H	H	83.8	134.9	-97.3	157.4	51.1	245.7	1.2606	1.3111
1b	H	NO_2	70.2	154.9	-84.3	158.3	84.7	242.6	1.2669	1.3178
1c	OMe	H	78.5	133.7	-95.7	157.4	55.1	253.2	1.2620	1.3135
1d	OMe	NO_2	63.9	152.0	-81.7	158.0	88.0	239.7	1.2689	1.3207
2a	H	H	74.9	154.4	-80.5	168.7	79.4	249.2	1.2624	1.3135
2b	OMe	H	70.6	154.1	-79.5	169.0	83.5	248.6	1.2637	1.3152
2c	F	H	81.1	151.4	-80.8	168.6	70.3	249.5	1.2612	1.3095
2d	H	OMe	75.9	143.8	-83.3	168.0	67.9	251.3	1.2616	1.3099
2e	H	NO_2	65.7	166.1	-72.1	169.3	100.4	241.4	1.2697	1.3218
2f	F	OMe	81.1	140.7	-83.4	168.2	59.5	251.7	1.2607	1.3068
2g	F	NO_2	168.0	-69.1	169.8	169.8	106.3	238.9	1.2682	1.3168
2h	OMe	OMe	71.4	144.2	-83.1	168.6	72.9	251.7	1.2628	1.3125
2i	OMe	NO_2	50.4	170.1	-65.7	168.0	119.7	233.7	1.2717	1.3253

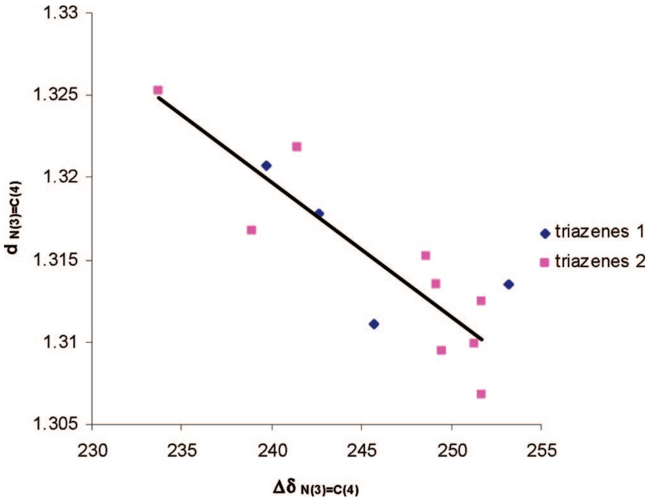


FIGURE 4. Correlation of bond lengths in Å and chemical shift differences $\Delta\delta$[N(3),C(4)] (ppm) of the partial N(3)=C(4) double bond in triazenes **1** and **2** ($d_{N(3)=C(4)} = -0.0008\Delta\delta_{N(3)=C(4)} + 1.5156$; $R^2 = 0.8033$).

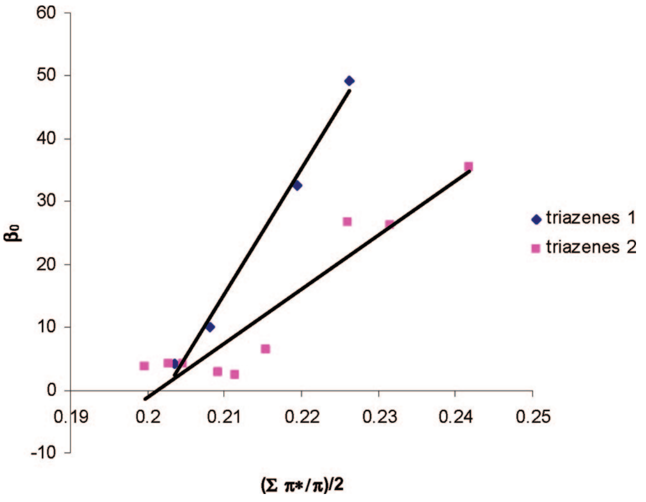


FIGURE 5. Correlation of molecular hyperpolarizability at zero frequency, β_0 (10^{-50} CV^{-2} m^3]) and mean of the sum of occupation coefficients π^*/π of the partial N(1)=N(2 and N(3)=C(4) double bonds in triazenes **1** ($\beta_0 = 1983.6\ (\Sigma\ \pi^*/\pi)/2 - 401.21$; $R^2 = 0.9912$) and **2** ($\beta_0 = 861.97(\Sigma\ \pi^*/\pi)/2 - 173.61$; $R^2 = 0.8871$).

N(3)=C(4) partial double bond: With increasing donor−acceptor character of the triazenes the bond length is elongated (cf. **4** in Scheme 3 and bond lengths in Table 2), the π-bond order will be appropriately reduced and the π-polarization of this partial N(3)=C(4) double bond should be increased.

However, $\Delta\delta(^{15}N,^{13}C_{N(3)=C(4)})$ values in **1** and **2** (cf. Figure 4) are not following the expected trend. There is no real correlation of $d_{N(3)=C(4)}$ versus $\Delta\delta(^{15}N,^{13}C_{N(3)=C(4)})$. The ^{13}C chemical shift of C-4 remains almost constant (as estimated as conjugation stopper in refs 13 and 14), changing by only $\Delta\delta = 0.9$ ppm (in **1**) and 1.3 ppm (in **2**), but $\delta(^{15}N)$ proves to be variable, indicating changes in π-bond polarization. The ^{15}N chemical shift of N(3) is lowfield shifted with increasing donor−acceptor character in both groups of compounds, however the correlation is of low quality (cf. Figure 4). Obviously, both $\delta_{C\text{-}4}$ and $\delta_{N\text{-}3}$ prove to be less useful to indicate the polarization of the partial N(3)=C(4) double bond. Obviously, the twist of the donor part of the molecules **1** and **2** from the common plane of resonance is the reason for the failing to indicate the corresponding polarization of the partial N(3)=C(4) double bond. In addition, other influences on the chemical shifts of both $\delta_{C\text{-}4}$ and $\delta_{N\text{-}3}$ (probably the γ-effect of the *N*-alkyl substituents) will be active, will contribute and cover the indication of the corresponding charge polarization by $\Delta\delta(^{15}N,^{13}C_{N(3)=C(4)})$.[22]

However, the results when comparing molecules **1** and **2** of the same substitution pattern (marked in Table 3) are congruent with the quotient considerations (vide supra); again the corresponding push−pull effect proves to be larger in the *N*-*t*-Bu compounds **2** than in the *N*-Me analogs **1**.

Summarizing the $\Delta\delta(^{15}N)$ results with respect to a useful sensor for quantifying both the push−pull effect and thereby the donor-acceptor character of certain compounds, the same result was obtained when employing similarly the ^{13}C chemical shifts of the central partial C=C double bond of push−pull olefins:[1,3,4b] only absolutely comparable structures (substitution differences only in δ-position to the partial double bond studied,[4] no steric hindrance influences) can be examined with respect to the donor−acceptor character of appropriately polarized molecules; in the case of the triazenes **1** and **2** $\Delta\delta(^{15}N)$ of the partial N(1)=N(2) double bond can be employed. Otherwise, $\Delta\delta$ fails as sensor of the push−pull effect, as $\Delta\delta(^{15}N,^{13}C)$ in the triazenes studied.

Potential NLO Application of Triazenes 1 and 2 Subject to Hyperpolarizability. With the two parameters (bond lengths $d_{N=N}$ and occupation quotients $\pi^*_{N=N}/\pi_{N=N}$ of partial N(1)=N(2) and N(3)=C(4) double bonds) in hand, quantifying the donor-accepter properties of the studied triazenes, the molecular hyperpolarizabilities at zero frequency, β_0, contained in Table 2, have been calculated and correlated with the mean of the sum of $\pi^*/\pi_{N(1)=N(2)}$ and the $\pi^*/\pi_{N(3)=C(4)}$ quotients for both partial N=N and C=N double bonds in **1** and **2**. A clear linear dependence of the two parameters in the triazenes **1** is apparent (Figure 5). A similar correlation is found for triazenes **2**; however, only the nitro group at phenyl and the methyoxy group at the donor moiety seem to be of major importance for the molecular hyperpolarizability of **2**. While the π^*/π quotients are still differentiating respect to the push−pull effect, the hyperpolarizabilty in **2a,c,d,f,h** and **2e,g**, respectively, remains almost constant. This is a strong hint that besides the donor−acceptor character of potential NLO molecules (characterized by bond length and occupation π^*/π quotient variations) there are further influences on both molecular hyperpolarizability and suitability for NLO applications.

The correlation of β_0 with the mean sum of the π^*/π quotients of the partial N=N and N=C double bonds in **1** and **2** represents a general structural parameter (the mean push−pull effect of the two conjugated partial double bonds) in the two rows of triazenes **1** and **2** that correlates with the molecular hyperpolarizability β_0 for the compounds. It is important to have an inherent parameter to use for assessing compounds as suitable NLO materials. Alternatively, the bond length, a parameter usually employed in discussing NLO property-structure relationships[23] due to structural changes, can also be employed along the series **1** and **2**. However, our recommendation is that the

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mean sum of the π^*/π quotients of the partial double bonds in the corresponding chromophore should be employed in characterizing the molecular hyperpolarizabilities of any compounds considered potentially useful as NLO materials. However, the molecular hyperpolarizability, characterized readily by the present structural parameters of chromophore **4**, is not the only desirable property for new organic NLO materials; there are molecules of better hyperpolarizabilities[24] and superior processing capabilities (e.g., sufficient thermal stability during melt growth) for current state-of-the-art materials.[25]

If employing, within this context, the donor−acceptor properties of the triazenes **1** and **2** studied along this research, triazenes **1b,d** and **2e,g,i** with $R^2 = NO_2$ can be strongly recommended for NLO application purposes.

Conclusions

Structures, occupations of antibonding π^* and bonding π orbitals of partial N═N and N═C double bonds and both ^{13}C and the ^{15}N chemical shifts of two rows of donor−acceptor triazenes **1** and **2**[12] (Scheme 2) were theoretically calculated on the B3LYP/6-311G** level of theory. The molecules are not completely flat but are twisted up to 30° in certain parts of the molecules. Both bond lengths $d_{N=N}$ and occupation quotients π^*/π of the partial N═N and N═C double bonds were found to be excellent and generally applicable sensors of the donor−acceptor character of these strongly polarized molecules.

The same result can be reported for $\Delta\delta(^{15}N_{N(1)=N(2)})$ but not for $\Delta\delta(^{15}N,^{13}C_{N(3)=C(4)})$ with respect to being useful sensors for quantifying both the push−pull effect and thereby the donor−acceptor character of these compounds. The situation is parallel to previous studies with ^{13}C NMR spectroscopy:[1,3,4b] only sufficiently comparable structures (substitution differences in δ-position to the partial double bond studied, no steric hindrance influences) can be examined.

Molecular hyperpolarizabilities at zero frequency, β_0, were calculated and correlated with the occupation quotients π^*/π of the partial N(1)═N(2) and N(3)═C(4) double bonds. Clear linear dependencies corroborate the occupation quotient to be a useful parameter to quantify the donor−acceptor character of these highly polarized molecules; however, sufficient donor−acceptor character of compounds is not the only but obviously one dominant requirement to recommend substances for NLO applications.

The triazene linker does not act as a conjugation stopper as was reported for the diazo bridge.[13,14,21,22] In the case of molecules **1**, in addition to bond length alternation, infrared active vibrations, dipole moments, and absorption wavelengths corroborate this final conclusion.[26]

Supporting Information Available: Bond lengths, bond angles, coordinates, and absolute energies at the B3LYP/6-311G** level of theory for the triazenes **1** and **2** studied. This material is available free of charge via the Internet at http://pubs.acs.org.

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