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Hyperpolarizability of donor–acceptor azines subject to push–pull character and steric hindrance

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ABSTRACT

The push–pull character of two series of donor–acceptor azines has been quantified by ^{13}C, ^{15}N chemical shift differences of the partial C(1)=N(1) and N(2)=C(2) double bonds in the central linking C(1)=N(1)–N(2)=C(2) unit and by the quotient of the occupations of the bonding π and anti-bonding π^* orbitals of these bonds. Excellent correlation of the latter push–pull parameter with the corresponding bond lengths $d_{C=N}$ strongly recommend both the occupation quotients π^*/π and the corresponding bond lengths as reasonable sensors for quantifying the *push*, *pull character* along the C=N–N=C linking unit, for the donor–acceptor quality of the two series of azines and for the molecular hyperpolarizability β_0 of these compounds. Within this context, reasonable conclusions concerning the interplay of steric hindrance in the chromophore, push–pull character and hyperpolarizability of the azines and their application as NLO materials will be drawn.

1. Introduction

Searching for organic materials with nonlinear optical (NLO) properties is usually concentrated on molecules with donor–acceptor π-conjugation (D–π–A) and deals with the systematic investigation of substituent effects on the degree of π-conjugation, steric hindrance and the hyperpolarizability of the substances. Besides, geometrical arrangement of the molecules in the solid state, their interaction, other physicochemical properties (e.g. strong intramolecular charge-transfer absorptions) and engineering possibilities are important.[1–11] At present, there is an insufficient understanding of all influences for designing optimal NLO materials, even if the influencing factors in certain classes of D–π–A compounds were theoretically studied.[12] Concerning especially the molecular effects of substituents (number, positional isomerism, donor/acceptor strength and combination, preferred conformations and, finally, solution),[6] more work is required because in this respect, there is generally only a singular combination of substituents that is most effective and the reason for this is not yet understood.

To quantify the *push–pull effect* in D–π–A compounds, bond length alternation (BLA) and out-of-plane distortions of the polarized C=C double bonds, available from X-ray studies, have been employed for a long time.[13] Alternatively, dipole moment measurements,[14] cyclic voltametry,[15] vibrational spectroscopy,[16] bond lengths[17] and barriers to rotation about the partial C=C double bonds[18] (from dynamic NMR studies), the ^{13}C chemical shift differences, $\Delta\delta_{C=C}$, of the carbon atoms of the polarized C=C double bonds[19] and the occupation quotients (π/π^{*}[20]) of the bonding (to quantify the acceptor activity) and anti-bonding orbitals (to quantify the donor activities) of these C=C double bonds were adopted. In the latter case, not only the push–pull effect in D–π–A compounds could be quantified, but also a linear dependence of the push–pull quotient (π^*/π) on molar hyperpolarizabilities of these compounds was detected.[21] Thus, π^*/π proves to be an easily accessible, general and sensitive parameter of the donor–acceptor quality of compounds for potential NLO applications, and in this context it could be successfully employed to characterize two sets of triazenes (**1** and **2**) in this context.[22] In opposite to the triazene linkage (=N–N=N–), which does not act as a *conjugation stopper*,[22,23] different results have been published for the similar azine bridge. The basic query concerns the situation whether[24–27] or not[28,29] the linking =N–N= group acts as a *conjugation stopper* by employing our approach.[19a,20] Therefore, several types of azines (Scheme 1) were theoretically studied at the DFT level of theory in which the linking azine unit should act either as conjugation stopper (**3**)[24–27] or show trends consistent with delocalization within the azine framework (**3h**, **3q**, **4**–**7**).[28,29]

2. Computational details

Theoretical calculations and the Natural Bond Orbital (NBO) population analysis[30] were performed using Gaussian03,[31] geometry

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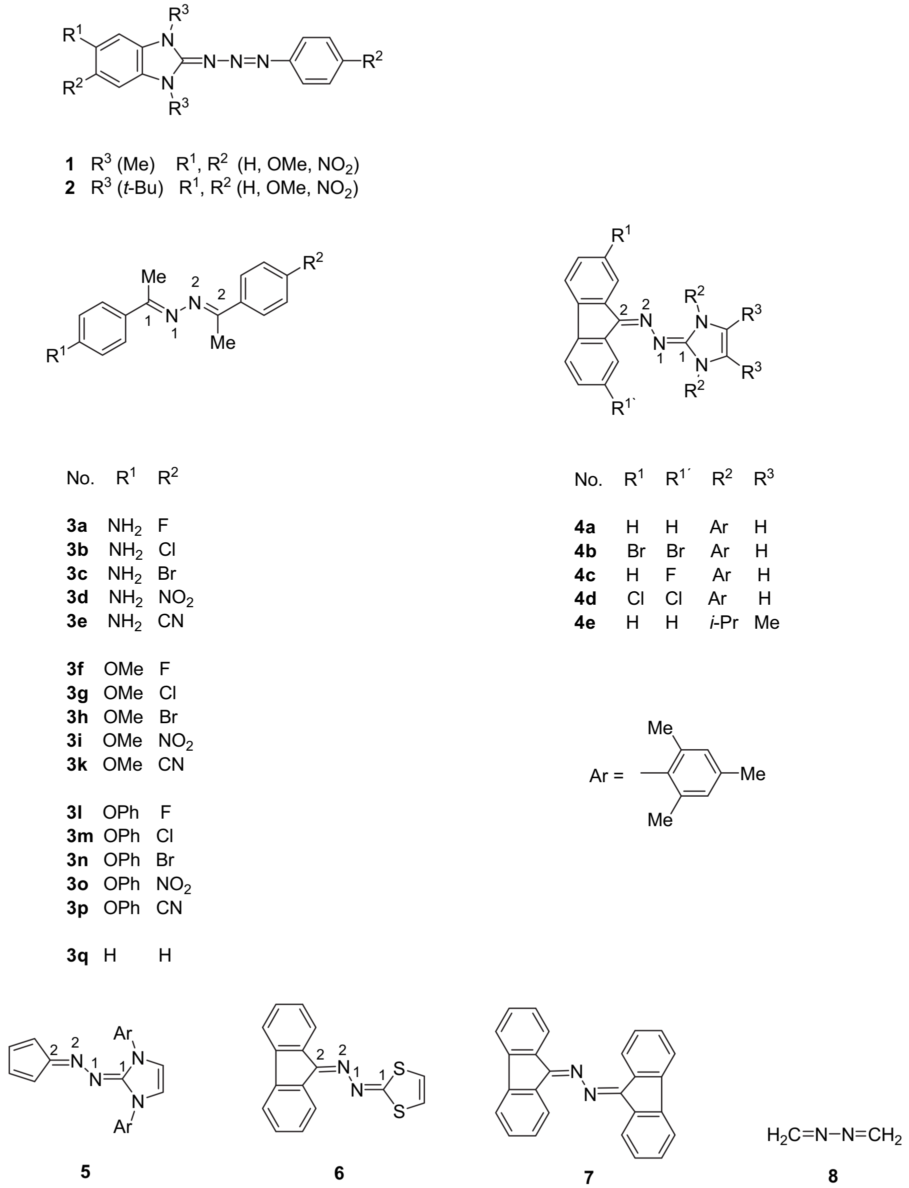


1 R^3 (Me) R^1, R^2 (H, OMe, NO_2)
2 R^3 (*t*-Bu) R^1, R^2 (H, OMe, NO_2)

No.	R^1	R^2
3a	NH_2	F
3b	NH_2	Cl
3c	NH_2	Br
3d	NH_2	NO_2
3e	NH_2	CN
3f	OMe	F
3g	OMe	Cl
3h	OMe	Br
3i	OMe	NO_2
3k	OMe	CN
3l	OPh	F
3m	OPh	Cl
3n	OPh	Br
3o	OPh	NO_2
3p	OPh	CN
3q	H	H

No.	R^1	$R^{1'}$	R^2	R^3
4a	H	H	Ar	H
4b	Br	Br	Ar	H
4c	H	F	Ar	H
4d	Cl	Cl	Ar	H
4e	H	H	*i*-Pr	Me

5 **6** **7** **8**

$H_2C=N-N=CH_2$

Scheme 1.

optimizations at the B3LYP/6-311G* level of theory without constraints.[32] The molecules **3**–**8** (see Scheme 1) are not completely flat but the azine group =N–N= is twisted from the common plane of resonance up to 41.6°; the twist angles are given in Table 1. The occupation of anti-bonding π^*, bonding π orbitals, the quotient π^*/π and the corresponding bond lengths *d*/Å of the partial $C^1{=}N^1$ and $N^2{=}C^2$ double bonds in the linking chain $C^1{=}N^1{-}N^2{=}C^2$ are given in Table 2. Molecular hyperpolarizabilities at zero frequency $\beta(0)$ 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[33] 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 $\Delta\delta$ (^{13}C,^{15}N) together with the corresponding bond lengths *d*/Å are given in Table 3.

Synthesis and characterization of azines **3**–**8** are published[24–29]; all calculations were carried out on SGI workstations and LINUX clusters.

3. Results and discussion

3.1. Steric hindrance in azines 3–8

The azines studied are partly flat (**4**–**6** and **8**) but in **3** and **10** the chromophore $C^1{=}N^1{-}N^2{=}C^2$ is clearly twisted from a common plane of resonance (cf. Table 1) up to 138.4° (in **3q**). In terms of non-restricted π-conjugation and developing the whole push–pull effect in these D–π–A compounds, this means considerable restriction in donor–acceptor character in **3** and **7** but almost full D–π–A activity in the other azines studied (**4**–**6** and **8**). Furthermore, the influence of the push–pull effect on the twist angle is readily visible in the structurally comparable compounds **3** and **4**: (i) In Glaser's donor–acceptor azines **3**, largest twist (138.4°) is observed in the non-substituted compound **3q** (R^1, R^2=H), while the twist angles proves

Table 1
Twist angle of the azine chromophore C=N–N=C in compounds **3–8**

No.	Twist angle (°)
3a	145.9
3b	145.0
3c	145.0
3d	145.2
3e	145.1
3f	144.9
3g	144.1
3h	143.8
3i	142.3
3k	143.0
3l	146.2
3m	145.7
3n	145.6
3o	143.8
3p	144.9
3q	138.4
4a	180.0
4b	177.7
4c	177.2
4d	180.0
4e	173.9
5	179.9
6	180.0
7	139.3
8	180.0

to be smaller (142.2°–146.2°) in the remaining azines **3**. The increasing push–pull effect (and hereby increasing D–π–A activity) improves the possibilities of π-conjugation and forces the involved π-bonds progressively into a common plane of resonance. (ii) Thus the amino group appears to be the most effective donor substituent (145.1°–145.9°) followed by the phenoxy (144.9°–146.2°) and the methoxy group (142.2–144.9°). (iii) The exact twist angle with respect to the three donor substituents is furthermore dependent on the corresponding acceptor substituent in the certain compound: (iv) In this sense, pairs NH_2/halogens and OPh/halogens prove to be the best combinations for reasonable D–π–A activity (145°–146.2°).

In the azines **4**, same conclusions can be drawn from the twist angles: Steric hindrance due to $R^2=i-Pr$ instead of R^2=Aryl reduces the π-conjugation in **4e** (173.9°) with respect to the other compounds **4** as do the halogens (as +M substituents) in **4b–d** (177.2–177.9°) with respect to **4a** which is completely flat (180°). The same results as for the latter compound can be reported for the azines **5**, **6** and **8**.

Resuming this paragraph, azines **3** and **7** are substantially twisted from a common plane of resonance in the chromophore C=N–N=C while azines **4–6** and **8** contain flat or almost flat chromophores for non-restricted π-conjugation. This should be of remarkable influence on the intensity of the push–pull effect in **3–8** and finally on the NLO properties of these compounds. It is interesting to learn whether these structural influences are indicated by parameters to quantify the push–pull effect and the NLO properties as well (vide infra).

3.2. Bond length and occupation coefficient for quantifying the push–pull effect in azines 3–8

The two push–pull parameters, bond lengths *d*/Å and occupation quotients π*/π, of the partial $C^1=N^1$ and $N^2=C^2$ double bonds in the donor–acceptor linking chain $C^1=N^1–N^2=C^2$ were considered; data are given in Table 2 and the corresponding values are correlated in Figures 1 and 2. The correlations are not excellent but point into the right direction: with increasing donor–acceptor character of the azines **3–8** (cf. Scheme 2), the two partial C=N double bonds are elongated – thereby the occupation quotients $\pi^*_{C\text{-}1=N\text{-}1}/\pi_{C\text{-}1=N\text{-}1}$ and $\pi^*_{N\text{-}2=C\text{-}2}/\pi_{N\text{-}2=C\text{-}2}$ increase due the parallel shift in D–π–A activity and hereby changes in π-bond orders (see data also in Table 2).

The same conclusions, with respect to the donor–acceptor character of the molecules **3–8**, can be drawn from the dipole moments of the compounds, additionally included in Table 2. Thus, the azines **3h**,**q** and **4–8** studied by Clyburne et al.[28,29] can be confirmed to be strongly polarized, π-delocalized materials which, in case extreme push–pull substitutions, should exhibit NLO behaviour.

However, there are some interesting additional conclusions from the data in Table 2 and Figures 1 and 2: (i) There is a notable outlier (**6**) in the $C^1=N^1$ correlation. This azine is the only one containing sulphur as donor atoms and, obviously, the level of theory applied is insufficient to compute adequately the structure for this compound. We recalculated the molecule on the MP2/6-311G** level of theory; the $C^1=N^1$ bond length is elongated to 1.306 Å which is in much better agreement with the correlation in Figure 2 (also the $C^2=N^2$ bond length was changed – 1.302 Å – but only slightly). Thus, the outlier azine **6** in Figure 1 is treated as a computational problem.

The second conclusion (ii) proves to be more interesting. The change in both bond lengths and occupation quotients of azines **3** is, compared with the other azines **4–8**, much smaller (in case of the partial $N^2=C^2$ double bond even negligible), which is in complete agreement with the results of Glaser et al.[24–27], which were obtained from ^{13}C NMR spectroscopy, X-ray analysis and theoretical studies and classifies the azine bridge as *conjugation stopper*. If the scale of the correlation *d* vs. π*/π is reduced (cf. Fig. 3) reasonable correlation is obtained for the partial $C^1=N^1$ double bond; for $N^2=C^2$ no correlation was obtained (cf. Fig. 2). As the reason therefore, steric hindrance within the azine chromophore C=N–N=C can be readily identified: Remarkable twist in **3** (138.4–146.2°) but unlimited π-conjugation in the other azines **4–8** (177.2–180°) makes the difference; the same is true for compound **7** (139.3°). The *conjugation stopper* actually is *not* the azine link between donor and acceptor part of the azines **3** but the *steric hindrance* within the molecules. This conclusion, however, must not necessarily mean that compounds with strongly sterically hindered chromophores as the azine group in compounds **3** are useless material for NLO applications (vide infra).

3.3. Chemical shift differences Δδ for quantifying the push–pull effect in azines 3–8

As Δδ (^{13}C) in push–pull olefins,[18,19,21] the chemical shift differences $\Delta\delta_{C\text{-}1=N\text{-}2}$ and $\Delta\delta_{N\text{-}2=C\text{-}2}$ in the azines **3–8** should be similarly useful sensors of the corresponding push–pull effect. Chemical shifts are given in Table 3 and are correlated in Figures 4 and 5 to the corresponding bond lengths, another reliable push–pull effect indicator (employed already in former correlations as given in Table 2 and Figs. 1–3). With increasing push–pull character of the partial C=N double bonds, bond elongation and increasing chemical shift differences $\Delta\delta_{C=N}$ were expected. The corresponding results, at best, are equivocal. While in for $C^1=N^1$, the correlation still points into the right direction, the direction of the remaining correlation for the $N^2=C^2$ partial double bond is reversed and thus meaningless; the azines **3** are completely independent (cf. Fig. 4). The $d_{C(1)=N(1)}$ vs. $\Delta\delta_{C(1)=N(1)}$ dependence (cf. Fig. 5) is not bad, but there is an outlier (**6**) (vide supra) and the azines **3**, on the other hand, develop their own dependence with the right direction and slope (cf. Fig. 6) but the range is very small, as found similarly in the corresponding occupation quotient correlation.

Summarizing the Δδ (^{15}N, ^{13}C) results with respect to a useful sensor for quantifying both the push–pull effect and hereby 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:[18,19,21]

Table 2
Occupation numbers of antibonding π^* and bonding π orbitals, bond lengths of the corresponding partial $C^1{=}N^1$ and $N^2{=}C^2$ double bonds, molecular hyperpolarizabilities at zero frequencies, $\beta(0)$, and dipole moments μ, of azines **3–8**

Compound	π	π^*	π^*/π	d(Å)	$\sum\pi^*/\pi/2$	$\beta(0)$ [10^{-50} CV^{-2} m^3]	μ [Debye]
	$C^1{=}N^1$						
3a	1.89840	0.20690	0.1090	1.2928	0.1056	12.2	3.11
3b	1.89812	0.20767	0.1094	1.2930	0.1057	14.8	3.54
3c	1.89559	0.20789	0.1097	1.2931	0.1063	14.8	3.43
3d	1.89177	0.21239	0.1123	1.2945	0.1073	50.5	7.57
3e	1.89509	0.21120	0.1114	1.2939	0.1069	30.3	7.05
3f	1.90074	0.19897	0.1047	1.2915	0.1030	6.7	3.25
3g	1.90040	0.19948	0.1050	1.2917	0.1029	8.3	3.65
3h	1.90081	0.19959	0.1050	1.2916	0.1030	8.0	3.61
3i	1.89801	0.20261	0.1067	1.2924	0.1037	35.5	6.40
3k	1.89838	0.20183	0.1063	1.2922	0.1036	20.9	4.90
3l	1.89852	0.1967	0.1036	1.2912	0.1025	6.7	2.09
3m	1.89783	0.19717	0.1039	1.2914	0.1024	8.5	2.60
3n	1.89780	0.19742	0.1040	1.2915	0.1023	8.0	2.52
3o	1.89566	0.19991	0.1055	1.2922	0.1029	37.9	6.31
3p	1.89542	0.19920	0.1051	1.2921	0.1029	22.8	5.71
3q	1.90663	0.18895	0.0991	1.2890	0.1000	0.83	1.26
	$N^2{=}C^2$						
3a	1.90107	0.19440	0.1023	1.2900			
3b	1.90002	0.19364	0.1019	1.2899			
3c	1.89938	0.19542	0.1029	1.2899			
3d	1.89092	0.19365	0.1024	1.2906			
3e	1.89466	0.19377	0.1023	1.2901			
3f	1.90177	0.19286	0.1014	1.2898			
3g	1.90061	0.19178	0.1009	1.2897			
3h	1.90120	0.19216	0.1011	1.2896			
3i	1.89433	0.19079	0.1007	1.2898			
3k	1.89611	0.19127	0.1009	1.2897			
3l	1.89965	0.19267	0.1014	1.2898			
3m	1.89831	0.19149	0.1009	1.2900			
3n	1.89785	0.19098	0.1006	1.2900			
3o	1.89272	0.18984	0.1003	1.2900			
3p	1.89384	0.19054	0.1006	1.2900			
	$C^2{=}N^2$						
4a	1.85154	0.28505	0.15395	1.2972	0.2085	11.2	5.24
4b	1.83695	0.30160	0.16418	1.2997	0.2207	11.7	5.67
4c	1.84815	0.28143	0.15227	1.2969	0.2059	11.3	5.21
4d	1.83900	0.30164	0.16402	1.2994	0.2203	12.1	5.56
4e	1.84429	0.31493	0.17075	1.3012	0.2321	14.8	6.69
5	1.81018	0.28074	0.15509	1.3036	0.2126	6.8	5.27
6	1.85862	0.23748	0.12777	1.2924	0.1689	10.3	1.79
7	1.86487	0.23399	0.12547	1.2899	0.1161	1.1	1.4
8	1.94390	0.05424	0.02790	1.2708	0.0279	0.01	0.0
	$N^1{=}C^1$						
4a	1.83273	0.48202	0.263007	1.3136			
4b	1.80637	0.50063	0.277147	1.3198			
4c	1.83493	0.47625	0.259547	1.3116			
4d	1.80725	0.49996	0.276641	1.3199			
4e	1.80688	0.53027	0.293473	1.3255			
5	1.80512	0.48764	0.270143	1.3169			
6	1.90290	0.39978	0.21009	1.2844			
7	1.89801	0.20261	0.106749	1.2899			
8	1.94390	0.05424	0.027903	1.2708			

Only absolutely comparable structures (substitution differences only in δ-position to the partial double bond studied,[19] no steric hindrance influences) can be examined respect to the donor–acceptor character of appropriately polarized molecules; in the case of the azines **3–8**, $\Delta\delta$ (^{15}N, ^{13}C) of the partial C=N double bonds cannot be generally employed and fails in case of $\Delta\delta$(C(1),N(1)) completely as sensor of the push–pull effect. If a certain group of compounds, however, as the azines **3** in this case, are compared subject to the push, pull effect, $\Delta\delta(N^1,C^1)$ could be a reliable substitute of the occupation quotient even if the variations in $d(N^1,C^1)$ and $\Delta\delta(N^1,C^1)$ are not very clear.

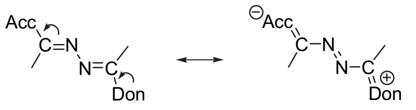
3.4. Potential NLO application of azines 3–8 subject to hyperpolarizability

With the two parameters (bond lengths $d_{C=N}$/Å and occupation quotients $\pi^*_{C=N}/\pi_{C=N}$ of partial $C^1{=}N^1$ and $N^2{=}C^2$ double bonds) in hand, quantifying the donor–accepter properties of the studied azines, the molecular hyperpolarizabilities at zero frequency β_0, contained in Table 2, have been calculated and correlated with the mean of the sum of $\pi^*/\pi_{C(1)=N(1)}$ and the $\pi^*/\pi_{N(2)=C(2)}$ quotients for both partial C=N double bonds in **3–8**. A clear linear dependence of the two parameters in the azines is apparent (Fig. 7), however, two dependences of different slopes were obtained: One for Glaser's azines **3** and a second one for all other azines **4–8** including **3h**,**q** which are near to the best line of fit for **4–8**. In addition, easy delocalization of π-electrons in the D–π–A azines **4–8** reveals only minor rising hyperpolarizability $\beta(0)$ up to 14.81 10^{-50} CV^{-2} m^3, while heavy steric hindrance and only rather small changes in the D–π–A character of the twisted azines **3** are accompanied by the extremely strong variance in hyperpolarizability β_0 (6.7–50.5×10^{-50} CV^{-2} m^3).

Obviously, the D–π–A activity of compounds for potential application as NLO material is important, but not deciding. Only

Table 3
Certain ^{15}N, ^{13}C chemical shifts (δ, ppm) of azines **3**–**8** calculated at the B3LYP/6-311G* level of theory

Compound	^{15}N/^{13}C chemical shifts							
	δ (C^1)	δ (N^1)	δ (N^2)	δ (C^2)	$\Delta\delta$ (C^1,N^1)	$\Delta\delta$ (N^2,C^2)	d/Å (C^1,N^1)	d/Å (N^2,C^2)
3a	166.4	−20.9	−7.7	164.0	187.3	171.7	1.2928	1.2900
3b	166.5	−21.2	−4.2	163.8	187.7	168.1	1.2930	1.2899
3c	166.5	−21.1	−4.0	164.0	187.7	168.0	1.2931	1.2899
3d	167.4	−21.4	9.8	163.7	188.8	153.9	1.2945	1.2906
3e	166.9	−21.7	5.7	163.5	188.6	157.7	1.2939	1.2901
3f	166.5	−17.3	−9.1	164.6	183.8	173.6	1.2915	1.2898
3g	166.6	−17.7	−5.8	164.4	184.4	170.2	1.2917	1.2897
3h	166.5	−17.7	−5.6	164.4	184.2	170.0	1.2916	1.2896
3i	167.0	−18.0	7.7	163.7	185.0	156.1	1.2924	1.2898
3k	167.1	−18.5	3.8	163.9	185.6	160.1	1.2922	1.2897
3l	166.5	−14.5	−10.2	165.4	181.1	175.7	1.2912	1.2898
3m	166.7	−15.1	−7.1	165.2	181.9	172.3	1.2914	1.2900
3n	166.8	−15.1	−6.9	165.3	181.9	172.2	1.2915	1.2900
3o	167.3	−16.0	6.4	164.4	183.4	158.0	1.2922	1.2900
3p	167.4	−16.4	2.4	164.8	183.8	162.4	1.2921	1.2900
3q	164.8	−8.3	−8.3	164.8	173.1	173.1	1.2890	1.2890
4a	156.2	−126.4	6.4	155.3	282.6	148.9	1.3136	1.2972
4c	154.9	−130.4	13.8	154.2	285.3	140.4	1.3116	1.2969
4e	154.8	−123.8	14.0	152.3	278.7	138.4	1.3255	1.3012
5	155.5	−109.9	43.1	169.4	265.4	126.2	1.3169	1.3036
6	188.0	−53.4	−5.1	163.3	241.4	168.4	1.2844	1.2924
7	161.4	0.4	0.4	161.4	161.0	161.0	1.2899	1.2899
8	158.5	35.0	35.0	158.5	123.5	123.5	1.2708	1.2708



Scheme 2.

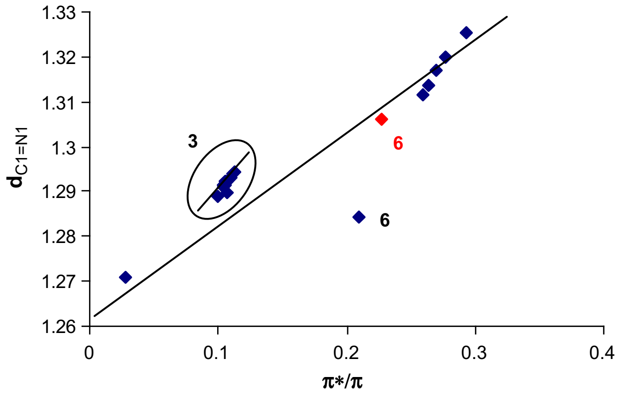


Figure 1. Correlation of bond lengths ($d_{C(1)=N(1)}$) in Å and occupation coefficients π^*/π of the partial C^1=N^1 double bond in azines **3**–**8**; (◆) **6** recalculated on basis of MP2/6-311G** geometry.

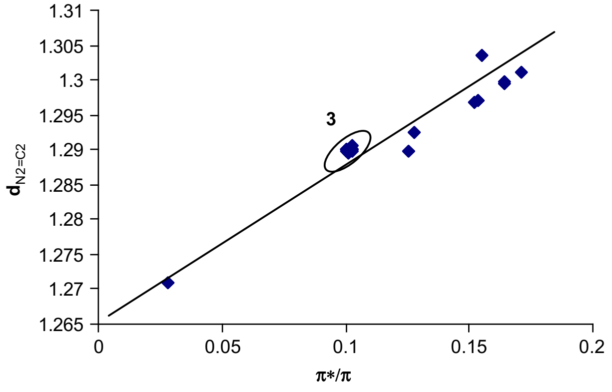


Figure 2. Correlation of bond lengths ($d_{N(2)=C(2)}$) in Å and occupation coefficients π^*/π of the partial N^2=C^2 double bond in azines **3**–**8**.

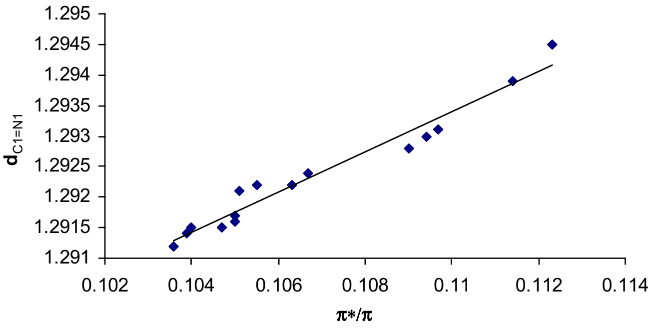


Figure 3. Correlation of bond lengths ($d_{C(1)=N(1)}$) in Å and occupation coefficients π^*/π of the partial C^1=N^1 double bond in azines **3**.

a small improvement in D–π–A activity (as in azines **3**) can result in strong change in hyperpolarizability of these compounds, while free π-conjugation in azines **4**–**8** and adequate heavy changes in D–π–A activity change $\beta(0)$ much less.

This conclusion is supported by Fig. 8, in which beside the $\beta(0)$ vs. $\sum\pi^*/\pi/2$ correlation of the azines **3** and **4**–**8** slopes, respectively (cf. Fig. 7), in addition, the corresponding dependences of two groups of triazenes **1** and **2**[22] (cf. Scheme 1) and some isophorones **9**[21] (cf. Scheme 3) are included. The triazenes **1** and **2** and isophorones **9**, respectively, are different in steric hindrance (**1** and **2** twisted, **9** planar), but the mean of the occupation quotients $\sum\pi^*/\pi/2$, as a measure of the d–π–A activity, changes only slightly while, dependent on the D–π–A substitution in the various compounds, strong changes in the hyperpolarizability of the studied compounds have been revealed. Thus, the D–π–A activity of molecules as material for potential NLO applications is important but not the size. Same conclusions can be drawn from the corresponding dipole moments of the compounds: molecules of higher hyperpolarizability have larger dipole moments but there is no general correlation [e.g. **4e** ($\beta(0)$=14.81×10^{-50} CV^{-2} m^3) has a larger dipole moment (μ=6.69 D) than **3i** ($\beta(0)$ 35.5×10^{-50} CV^{-2} m^3), μ=6.40 D]

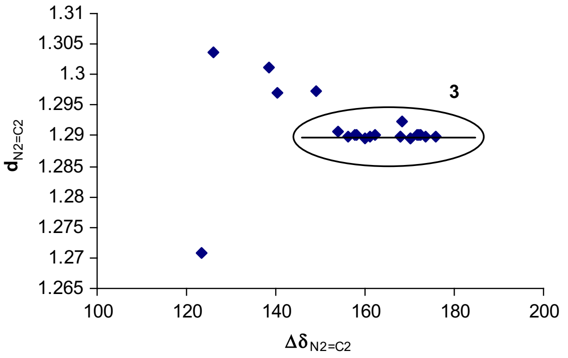


Figure 4. Correlation of bond lengths ($d_{N(2)=C(2)}$)) in Å and ^{15}N, ^{13}C chemical shift differences $\Delta\delta$(N(2),C(2) (ppm) of the partial N(2)=C(2) double bond in the azines **3–8**.

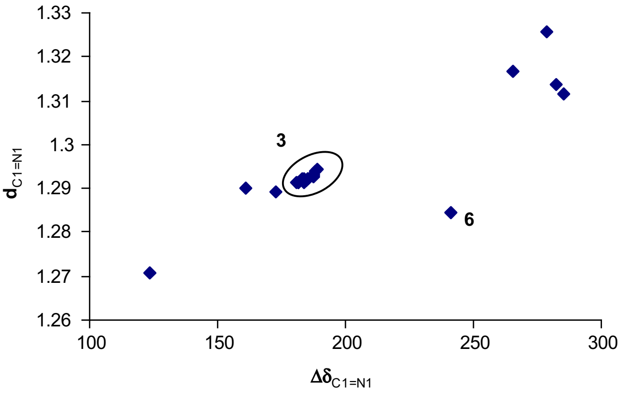


Figure 5. Correlation of bond lengths ($d_{C(1)=N(1)}$)) in Å and ^{13}C, ^{15}N chemical shift differences $\Delta\delta$(C(1),N(1) (ppm) of the partial C(1)=N(1) double bond in the azines **3–8**.

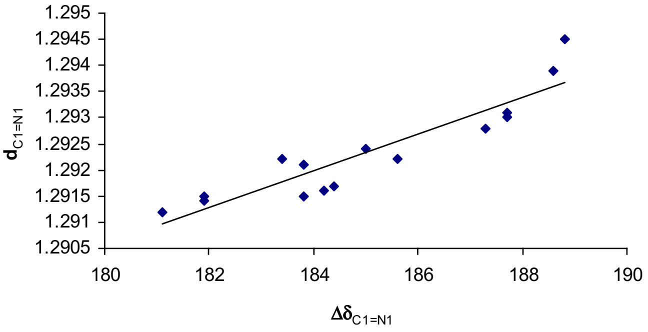


Figure 6. Correlation of bond lengths ($d_{C(1)=N(1)}$)) in Å and ^{13}C, ^{15}N chemical shift differences $\Delta\delta$(C(1),N(1) (ppm) of the partial C(1)=N(1) double bond in the azines **3**.

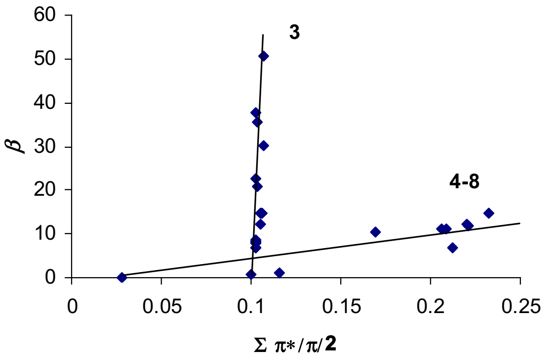


Figure 7. Correlation of molecular hyperpolarizability at zero frequency β_0 (10^{-50} CV^{-2} m^3) and mean of the sum of occupation coefficients $\pi*/\pi$ of the partial C(1)=N(1) and C(2)=N(2) double bonds in azines **3–8**.

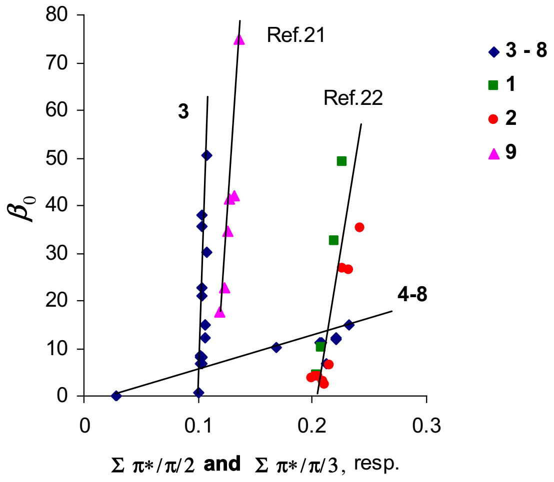
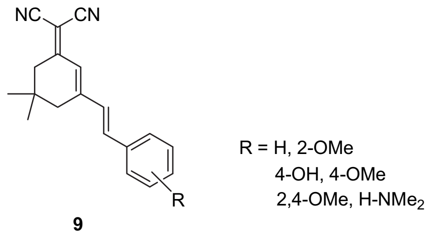


Figure 8. Correlation of molecular hyperpolarizability at zero frequency β_0 (10^{-50} CV^{-2} m^3) and mean of the sum of occupation coefficients $\pi*/\pi$ of the partial C(1)=N(1) and C(2)=N(2) double bonds in azines **3–8**, triazenes **1** and **2**,[22] and in isophorones **9**.[21]



Scheme 3.

but the hyperpolarizability proves to be much higher. This is a reasonable hint that besides the donor–acceptor character of potential NLO molecules (characterized by bond lengths, occupation $\pi*/\pi$ quotients and dipole moment variations) there are further (obviously, the deciding) influences on both molecular hyperpolarizability and suitability of the corresponding molecules for NLO applications.

4. Conclusions

Structures, occupations of anti-bonding $\pi*$ and bonding π orbitals of partial C=N double bonds and both ^{13}C and the ^{15}N chemical shifts of two rows of donor–acceptor azines **3** and **4–8** (Scheme 1) were theoretically calculated on the B3LYP/6-311G* level of theory. The molecules are not completely flat but twisted up to 42° from the common plane of π-delocalization. Both bond lengths $d_{N=N}$/Å and occupation quotients $\pi*/\pi$ of the partial C=N double bonds in the azine chromophore were found to be generally applicable sensors of the donor–acceptor character of these strongly polarized molecules. The same result cannot be reported for $\Delta\delta$ (^{13}C=^{15}N) another expected useful sensor for quantifying both the push–pull effect and thus the donor–acceptor character of these compounds.[18–20]

Molecular hyperpolarizabilities at zero frequency β_0 were calculated and correlated with the occupation quotients $\pi*/\pi$ of the partial C=N double bonds: Clear linear dependences corroborate the occupation quotient to be a useful parameter to quantify the donor–acceptor character of these highly polarized molecules; however, the donor–acceptor character of D–π–A compounds is not the only and even not the dominant requirement to recommend substances for NLO applications.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.09.026.

References and notes

1. Nicoud, J. F.; Twieg, R. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, NY, 1987; p 227.
2. Osaka, H.; Ishida, T.; Nogami, T.; Yamazaki, R.; Yasui, M.; Iwasaki, F.; Mizuguchi, A.; Kubata, M.; Uemiya, T.; Nisjimuru, A. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 918.
3. Mahanalingam, K.; Nethaji, M.; Das, P. K. J. *Mol. Struct.* **1996**, *378*, 177.
4. Favini, G.; Gamba, A.; Todeschine, R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 915.
5. Inoue, S.; Aso, Y.; Otsubo, T. *J. Chem. Soc., Chem. Commun.* **1997**, 1105.
6. Fabian, W. M. F.; Dworczak, R.; Junek, H.; Pawar, B. N. *J. Chem. Soc., Perkin Trans. 2* **1995**, 903.
7. Wortmann, R.; Lundquist, P. M.; Twieg, R. J.; Geletneky, C.; Moylan, C. R.; Jia, Y.; DeVoe, R. G.; Burland, D. M.; Bernal, M.-P. *Appl. Phys. Lett.* **1996**, *69*, 1657.
8. Khramov, D. M.; Bielawski, C. W. *J. Org. Chem.* **2007**, *72*, 9407; Khramov, D. M.; Bielawski, C. W. *Chem. Commun.* **2005**, 4859.
9. Strutz, S. J.; Hayden, L. M. *Appl. Phys. Lett.* **1999**, *74*, 2749.
10. He, M.; Leslie, T. M.; Sinicropi, J. A.; Garner, S. M.; Reed, L. D. *Chem. Mater.* **2002**, *14*, 4669.
11. Kwon, O.-P.; Ruiz, B.; Choubey, A.; Mutter, L.; Schneider, A.; Jazbinsek, M.; Gramlich, V.; Günter, P. *Chem. Mater.* **2006**, *18*, 4049.
12. Koch, R.; Finnerty, J. J.; Bruhn, T. *J. Phys. Org. Chem.* **2008**, *21*, 954.
13. See e.g. Ye, G.; Henry, W. P.; Chen, C.; Zhou, A.; Pittman, C. U., Jr. *Tetrahedron Lett.* **2009**, *50*, 2135 and references therein.
14. See e.g. Mitchell, D. M.; Morgan, P. J.; Pratt, D. W. *J. Phys. Chem. A* **2008**, *112*, 12597 and references therein.
15. Priego, E. M.; Sánchez, L.; Herranz, M. A.; Martín, N.; Viruela, R.; Ortí, E. *Org. Biomol. Chem.* **2007**, *5*, 1201 and references therein.
16. Abraham, J. P.; Sajan, D.; Shettigar, V.; Dharmaprakash, S. M.; Němec, I.; Hoe, I. H.; Jayakumar, V. S. *J. Mol. Struct.* **2009**, *917*, 27 and references therein.
17. Rattananakin, P.; Pittman, C. U., Jr.; Collier, W. E.; Daebø, S. *Struct. Chem.* **2007**, *18*, 399 and references therein.
18. Fischer, G.; Rudorf, W.-D.; Kleinpeter, E. *Magn. Reson. Chem.* **1991**, *29*, 204.
19. (a) Kleinpeter, E.; Klod, S. *J. Org. Chem.* **2004**, *69*, 4317; (b) Kleinpeter, E.; Thomas, St.; Uhlig, G.; Rudorf, W.-D. *Magn. Reson. Chem.* **1993**, *31*, 714.
20. Kleinpeter, E.; Schulenburg, A. *Tetrahedron Lett.* **2005**, *46*, 5995.
21. Kleinpeter, E.; Koch, A.; Mikhova, B.; Stamboliyska, B. A.; Kolev, T. M. *Tetrahedron Lett.* **2008**, *49*, 1323.
22. Kleinpeter, E.; Stamboliyska, B. A. *J. Org. Chem.* **2008**, *73*, 8250.
23. Preat, J.; Michaux, C.; Lawelle, A.; Perpète, E. A.; Jacquemin, D. *Chem. Phys. Lett.* **2008**, *451*, 37.
24. Chen, G. S.; Anthamatten, M.; Barnes, C. L.; Glaser, R. *J. Org. Chem.* **1994**, *59*, 4336.
25. Glaser, R.; Chen, G. S. *J. Comput. Chem.* **1998**, *19*, 1130.
26. Lewis, M.; Glaser, R. *J. Org. Chem.* **2002**, *67*, 1441.
27. Glaser, R.; Chen, N.; Wu, H.; Knotts, N.; Kaupp, M. *J. Am. Chem. Soc.* **2004**, *126*, 4412.
28. Hopkins, J. M.; Bowdridge, M.; Robertson, K. A.; Cameron, T. S.; Jenkins, H. A.; Clyburne, J. A. C. *J. Org. Chem.* **2001**, *66*, 5713.
29. Choytun, D. D.; Langlois, L. D.; Johansson, T. P.; MacDonald, C. L. B.; Leach, G. W.; Weinberg, N.; Clyburne, J. A. C. *Chem. Commun.* **2004**, 1842.
30. Bohmann, J. A.; Weinhold, F.; Farrar, T. C. *J. Chem. Phys.* **1997**, *107*, 1173.
31. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision C.02*, Gaussian, Inc.: Wallingford, CT, 2004.
32. Hehre, J. W.; Radom, L.; Ragué Schleyer, P. v.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley & Sons: New York, NY, 1986.
33. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.