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Quantification of the push–pull character of azo dyes and a basis for their evaluation as potential nonlinear optical materials

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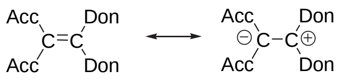
ABSTRACT

The push–pull characters of a large series of donor–acceptor substituted azo dyes—71 structures in all—have been quantified by the N═N double bond lengths, $d_{N=N}$, the ^{15}N NMR chemical shift differences, $\Delta\delta_{15N}$, of the two nitrogen atoms and the quotient, $\pi*/\pi$, of the occupations of the antibonding $\pi*$, and bonding π orbitals of this partial N═N double bond. The excellent correlation of the occupation quotients with the bond lengths strongly infers that both $\pi*/\pi$ and $d_{N=N}$ are excellent parameters for quantifying charge alternation in the push–pull chromophore and the molecular hyperpolarizability, β_0, of these compounds. By this approach, selected compounds can be appropriately considered as viable candidates for nonlinear optical (NLO) applications.

1. Introduction

The charge polarization of C═C double bonds[1] arising from the placement of electron-donating substituents at one end of the double bond and electron-withdrawing groups at the other end, so-called push–pull chromophores (cf. Scheme 1), can be easily quantified by either the bond length,[2] $d_{C=C}$, of the partial C═C double bond or the ^{13}C NMR chemical shift difference,[3] $\Delta\delta_{13C}$, of the two carbon nuclei constituting the bond. Rising push–pull character, which causes the charge polarization, results in an increase in the magnitude of both $d_{C=C}$ and $\Delta\delta_{13C}$.[4]



Scheme 1. Push–pull alkenes.

In addition to these two parameters to quantify the push–pull character of a compound, either quantification of the restricted rotation about the partial C═C double bond[2,5] or the occupation quotient $\pi*/\pi$ of this bond can be alternatively employed.[6,7] Interestingly, since electron-donating substituents release π-electron density into the antibonding $\pi*$ orbital of the C═C double bond whilst electron withdrawing substituents detract π-electron density from the bonding π orbital of the C═C double bond, both effects tend to elongate the C═C double bond. Of note, whilst the application of the bond length is restricted to solid-state measurements, viz. X-ray diffraction, studying the barrier to rotation using NMR is limited by the NMR timescale to a window of 80–100 kJ mol^{-1} for the corresponding barrier, $\Delta G^{\#}$,[5,6] and, furthermore, employing $\Delta\delta_{13C}$ is restricted to identical α,β-substitution patterns of the C═C double bond.[3] However, the occupation quotient $\pi*/\pi$ of the partial C═C double bond has proven to be a reliable and generally applicable parameter to quantify the *push–pull effect* in these kind of compounds[7] and has been successfully used for the characterization of normal and vinylogeous thio(seleno)amides,[8] fulvalenes,[9] vinylogous calicenes,[10] and push–pull alkynes[11,12] such as tolanes.[13]

Due to the fact that polarized push–pull chromophores (Don–π–Acc) typically possess large molecular dipoles, often have extremely high molecular hyperpolarizabilities,[14–18] β_0, and also exhibit strong intramolecular charge transfer bands,[19] these compounds consequently are promising candidates for specialized applications such as nonlinear optical (NLO) materials.[16] Azobenzene derivatives in particular, and pyridyl analogues especially, are of continuing interest for finding push–pull chromophore systems

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with suitable properties for applications in various devices such as organic thin-film transistors,[20] holographic information storage units,[21] and, as already implied, those requiring the use of NLO materials.[22] Of note, the important role that the aromatic/heteroaromatic moieties at the azo group play have been investigated.[23–25] However, organic chromophores with large molecular hyperpolarizabilities are not guaranteed to yield high quality organic NLO materials because the β_0 values must transfer into high macroscopic NLO activities in the end polymers,[26] though high β_0 values are obviously a starting requirement. Correlations of $\pi*/\pi$ and β_0, which are able to not only effect the occupation quotient as a useful indicator of the *push–pull effect*, but also the inherent hyperpolarizability of a Don–π–Acc, are of considerable interest.[27–29]

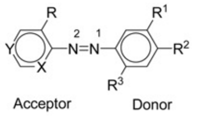
The aim of this paper is to extend our studies of the *push–pull effect* to a series of donor–acceptor azobenzene derivatives **1**–**4** (Scheme 2) recently reported by Kreicberga et al.[30] and to address the following considerations: (i) Can ^{15}N NMR chemical shift differences, $\Delta\delta_{15N}$, in **1**–**5** be employed similarly as was $\Delta\delta_{13C}$ for push–pull alkenes to quantify the donor–acceptor character[3,6,7] of these Don–π–Acc compounds? and (ii) can the occupation quotient, $\pi*/\pi$, be similarly employed to quantify the *push–pull effect* in these compounds? For this study, ^{15}N NMR chemical shifts, δ_{15N}, were measured for the experimentally available compounds **1**–**4** and the occupation quotients, $\pi*/\pi$, molecular hyperpolarizabilities, β_0, N═N double bond lengths, $d_{N═N}$, as well as the δ_{15N} of compounds **1**–**5** calculated. Attempts were then made to quantify the donor–acceptor properties of these compounds using these parameters. With the quantified push–pull characters of azobenzenes **1**–**5** in hand, additional aspects were also considered, viz. (iii) the effect of azobenzene substitution, (iv) the interrelationship between β_0 and the push–pull character of **1**–**5** and (v) evaluation of the structures with the most promising NLO application potentials.

2. Results and discussion

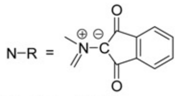
2.1. Experimental and computed ^{15}N NMR chemical shifts, δ_{15N}, of 1–5

The δ_{15N} of the available azobenzenes **1**–**4** (Scheme 2) were measured and unequivocally assigned via multiple bond correlations using HMBC experiments, including four-bond couplings, to facilitate indirect measurement of the insensitive ^{15}N nucleus in a practical manner.[31–33] The δ_{15N} values were also calculated using the GIAO method[34] by DFT at the B3LYP/6-311G**//B3LYP/6-311G** level of theory with both pairs of values, experimental and calculated, presented in Table 1.

From the geometry optimizations it was found that the structures of **1**–**4** are not necessarily completely or near planar and can be twisted by up to 66° with respect to the plane of the central N═N double bond (the dihedral angles, *Φ*, for the N═N–C$_i$–C$_o$ segments are presented in Table 1 to represent this distortion and as an indication of the steric hindrance in effect). However, the experimental and calculated δ_{15N} values were also correlated (Fig. 1) whereby, noting that calculated δ_{15N} values are typically larger than their experimental values, the correlation obtained is clearly sufficiently linear (R^2=0.8927) and hence provides strong evidence for accurately computed structures. Thus, the number of azobenzene derivatives was expanded by 47 structures (cf. Scheme 2) in order to obtain a comprehensive set for comparative study. The δ_{15N} for all 71 azo dyes **1**–**5** are presented in the Supplementary data section together with the dihedral angles, *Φ*, of the N═N–C$_i$–C$_o$ segments. Hereon in, only calculated δ_{15N} values have been used for analysis.



No.	X	Y	R	R^1	R^2	R^3
1a	**N**	**CNO_2**	**H**	**OC_8H_{17}**	**$N(CH_2CH_2OH)_2$**	**H**
1b	N	CNO_2	H	H	$N(CH_2CH_2OH)_2$	OC_8H_{17}
1c	**N**	CBr	H	H	$N(CH_2CH_2OH)_2$	OC_8H_{17}
1d	N	CNO_2	H	OMe	$N(CH_2CH_2OH)_2$	H
1e	N	CNO_2	H	OMe	$N(CH_2CH_2OH)_2$	H
1f	N	CNO_2	H	OMe	$N(CH_2CH_2OH)_2$	OMe
1g	N	CBr	H	OC_8H_{17}	$N(CH_2CH_2OH)_2$	H
1h	N	CBr	H	H	$N(CH_2CH_2OH)_2$	OMe
1i	N	CBr	H	OMe	$N(CH_2CH_2OH)_2$	H
1k	N	CBr	H	OMe	$N(CH_2CH_2OH)_2$	OMe
1l	N	CNO_2	H	H	H	H
2a	**N→O**	**CNO_2**	**H**	**OC_8H_{17}**	**$N(CH_2CH_2OH)_2$**	**H**
2b	N→O	CNO_2	H	OC_8H_{17}	$N(CH_2CH_2OH)_2$	OC_8H_{17}
2c	N→O	CBr	H	H	$N(CH_2CH_2OH)_2$	H
2d	**N→O**	**CBr**	**H**	**H**	**$N(CH_2CH_2OH)_2$**	**OC_8H_{17}**
2e	**N→O**	**CBr**	**H**	**OMe**	**$N(CH_2CH_2OH)_2$**	**OMe**
3a	**CCN**	**CNO_2**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
3c	**CCN**	**CNO_2**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**OC_8H_{17}**
3d	**CCN**	**CNO_2**	**CN**	**OC_8H_{17}**	**$N(CH_2CH_2OH)_2$**	**H**
3e	**CH**	**CNO_2**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
3f	**CH**	**CNO_2**	**CN**	**OMe**	**$N(CH_2CH_2OH)_2$**	**H**
3g	**CH**	**CNO_2**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**OMe**
3h	**CH**	**CNO_2**	**CN**	**OMe**	**$N(CH_2CH_2OH)_2$**	**OMe**
3i	**CH**	**CNO_2**	**H**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
3k	**CH**	**CNO_2**	**H**	**OMe**	**$N(CH_2CH_2OH)_2$**	**H**
3l	**CH**	**CNO_2**	**H**	**H**	**$N(CH_2CH_2OH)_2$**	**OMe**
3m	**CH**	**CNO_2**	**H**	**OMe**	**$N(CH_2CH_2OH)_2$**	**OMe**
3n	**CH**	**CNO_2**	**H**	**OC_8H_{17}**	**$N(CH_2CH_2OH)_2$**	**H**
3o	**CH**	**CNO_2**	**H**	**H**	**$N(CH_2CH_2OH)_2$**	**OC_8H_{17}**
3p	CCN	CNO_2	CN	OMe	$N(CH_2CH_2OH)_2$	H
3q	CCN	CNO_2	CN	H	$N(CH_2CH_2OH)_2$	OMe
3r	CCN	CNO_2	CN	OMe	$N(CH_2CH_2OH)_2$	OMe
3s	CH	CNO_2	CN	OC_8H_{17}	$N(CH_2CH_2OH)_2$	H
3t	CH	CNO_2	CN	H	$N(CH_2CH_2OH)_2$	OC_8H_{17}
3u	CH	CH	H	OC_8H_{17}	$N(CH_2CH_2OH)_2$	H
3v	CH	CH	H	H	$N(CH_2CH_2OH)_2$	OC_8H_{17}
3w	CH	CH	H	H	$N(CH_2CH_2OH)_2$	OMe
3x	CH	CH	H	OMe	$N(CH_2CH_2OH)_2$	OMe
3y	CH	CH	H	OMe	$N(CH_2CH_2OH)_2$	H
3z	CH	CNO_2	H	H	H	H
3aa	CCN	CNO_2	CN	H	H	H
3ab	CH	CNO_2	CN	H	H	H
3ac	CH	CH	H	OMe	$N(CH_2CH_2OH)_2$	OMe
3ad	CCN	CH	CN	OMe	$N(CH_2CH_2OH)_2$	OMe
3ae	CH	CNO_2	H	H	OMe	H
3af	CH	CNO_2	H	H	Me	OMe
3ag	CH	CNO_2	H	OMe	Me	Me
3ah	CH	CNO_2	H	Me	OMe	H
3ai	CCN	CNO_2	CN	Me	OMe	Me
4a	**CBr**	**N**	**Br**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4b	CBr	N	CN	H	$N(CH_2CH_2OH)_2$	H
4c	CCN	N	Ph	H	$N(CH_2CH_2OH)_2$	H
4d	CPh	N	Ph	H	$N(CH_2CH_2OH)_2$	H
4e	CCN	N	CN	H	$N(CH_2CH_2OH)_2$	H
4f	CBr	N	Ph	H	$N(CH_2CH_2OH)_2$	H
4g	**CPh**	**N**	**Ph**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4h	**CBr**	**N**	**Br**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4i	**CCN**	**N**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4k	**CPh**	**N**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4l	**CBr**	**N**	**CN**	**H**	**$N(CH_2CH_2OH)_2$**	**H**
4m	CPh	N	Ph	OMe	$N(CH_2CH_2OH)_2$	H
4n	CPh	N	Ph	H	$N(CH_2CH_2OH)_2$	OMe
4o	CPh	N	Ph	OMe	$N(CH_2CH_2OH)_2$	OMe
4p	CPh	N	Ph	OC_8H_{17}	$N(CH_2CH_2OH)_2$	H
4q	CPh	N	Ph	H	$N(CH_2CH_2OH)_2$	OC_8H_{17}
4r	CCH	N	H	H	H	H
4s	CCN	N	CN	H	H	H
4t	CBr	N	Br	H	H	H
4u	CPh	N	Ph	H	H	H
5a	CPh	N–R	Ph	H	$N(CH_2CH_2OH)_2$	H
5b	CBr	N–R	Br	H	$N(CH_2CH_2OH)_2$	H



N.b. Entries in bold are compounds that have been experimentally available for this study.

Scheme 2. Structures of studied compounds.

2.2. ^{15}N NMR chemical shift differences, $\Delta\delta_{15N}$, and the *push–pull effect* in 1–5

The ^{15}N NMR chemical shift differences, $\Delta\delta_{15N}$, of the two nitrogen atoms of the azo group as a measure of the *push–pull effect* in **1**–**4**, were evaluated for the experimentally available compounds. Both experimental and the corresponding calculated values are presented in Table 1; calculated values for all compounds

Table 1
Experimental [δ/ppm; nitromethane (ext.)] and calculated ^{15}N NMR chemical shifts [cf. Experimental], δ_{15N}, and calculated N=N bond lengths, $d_{N=N}$, dihedral angles, Φ, in the N=N–C$_i$–C$_o$ segments, occupation quotients, π^*/π, and molecular hyperpolarizabilities, β_0, of the experimentally available azobenzenes **1**–**4**

	δ_{N2} (ppm)[a]	δ_{N1} (ppm)[a]	$\Delta\delta$ (ppm)[b]	$d_{N=N}$ (Å)	Φ of N=N–C$_i$–C$_o$ (°)		π^*/π	$\beta_0\times10^{-50}$ (C.V^{-2} m^3)
					∢ (Acc)	∢ (Don)		
1a	140.7 (186.62)	86.2 (134.06)	54.5 (52.6)	1.2637	176.55	178.41	0.1345	59.8
2a	122.6 (165.60)	52.7 (98.98)	69.9 (66.6)	1.2710	176.45	178.69	0.1631	95.5
2d	120.8 (148.18)	69.4 (92.59)	51.4 (55.6)	1.2697	179.31	178.13	0.1602	21.9
2e	97.3 (143.68)	58.9 (84.69)	38.4 (59.0)	1.2715	178.76	178.52	0.1686	27.3
3a	129.5 (184.81)	37.0 (79.54)	92.5 (105.3)	1.2716	172.81	179.02	0.1751	79.2
3c	114.1 (172.03)	14.0 (61.73)	100.1 (110.3)	1.2768	165.70	177.93	0.1911	63.9
3d	127.1 (182.45)	18.0 (80.85)	109.1 (101.6)	1.2721	178.61	178.82	0.1784	93.0
3e	130.7 (174.68)	59.0 (99.45)	71.7 (75.2)	1.2672	178.50	178.38	0.1537	77.0
3f	132.2 (169.70)	67.6 (94.25)	64.6 (75.5)	1.2688	179.95	179.42	0.1612	88.2
3g	119.6 (168.42)	41.1 (88.95)	78.5 (79.5)	1.2704	179.33	178.39	0.1625	66.7
3h	114.0 (160.73)	42.0 (78.46)	72.0 (82.3)	1.2736	179.37	178.63	0.1756	75.3
3i	129.6 (168.17)	81.2 (118.82)	48.4 (49.4)	1.2623	179.62	178.95	0.1373	67.9
3k	132.3 (171.86)	92.3 (126.74)	40.0 (45.1)	1.2613	179.57	179.00	0.1334	79.2
3l	103.2 (167.37)	69.5 (107.24)	33.7 (60.1)	1.2651	179.52	177.68	0.1443	61.1
3m	121.9 (161.35)	74.6 (100.23)	47.3 (61.1)	1.2670	179.09	178.69	0.1529	69.6
3n	132.3 (171.45)	91.8 (124.65)	40.5 (46.8)	1.2616	179.21	179.49	0.1347	80.3
3o	123.8 (165.51)	68.5 (107.83)	55.3 (57.7)	1.2650	179.35	179.53	0.1439	56.9
4a	130.2 (202.65)	88.8 (129.14)	41.4 (73.5)	1.2584	131.90	177.30	0.1228	25.9
4g	176.1 (191.32)	103.8 (159.52)	72.3 (31.8)	1.2533	113.98	178.37	0.1048	18.4
4h	200.6 (201.49)	89.8 (125.63)	110.8 (75.9)	1.2589	131.11	178.90	0.1247	26.9
4i	133.2 (186.84)	38.7 (80.45)	94.5 (106.4)	1.2708	177.43	178.86	0.1709	39.5
4k	139.6 (183.92)	72.4 (104.74)	67.2 (79.2)	1.2639	151.81	179.98	0.1452	32.5
4l	139.2 (186.99)	62.4 (96.85)	76.8 (90.1)	1.2661	154.40	179.58	0.1525	35.4

[a] First entry, experimental values; second entry in parentheses, calculated values.

[b] First entry, NMR chemical shift differences, $\Delta\delta_{N2-N1}$, of the experimental δ_{15N} values; second entry in parentheses, differences of the calculated δ_{15N} values.

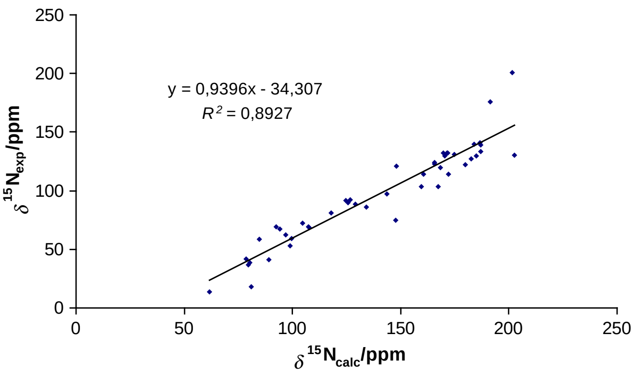


Figure 1. Correlation of experimental vs calculated ^{15}N NMR chemical shifts, δ_{15N}, for the experimentally available compounds **1**–**4**.

studied are given in the Supplementary data section. The correlation of all calculated $\Delta\delta_{15N}$ values vs the corresponding bond lengths, $d_{N=N}$, of the partial N=N double bond is portrayed in Figure 2. In contrast to the push–pull alkenes,[5–7] the correlation is comparatively poor because δ_{15N} are dependent on a number of factors[31–33] and charge polarization of the N=N double bond due to the *push–pull effect* is but one of them. The outstanding inference is that $\Delta\delta_{15N}$ is not a useful general parameter—without constraints—for evaluation of push–pull character. There is, nonetheless, a correct tendency (increasing $\Delta\delta_{15N}$ with growing bond length $d_{N=N}$), but the scatter of values clearly limits the ability to draw any firm conclusions. However, if structural variations are taken into account and the altering push–pull character of the differently substituted azobenzene derivatives considered by subdividing the compounds into four sets comprising **1** (Acc=2-pyridyl), **2** (Acc=2-pyridyl-*N*-oxide), **3** (Acc=substituted benzene), and {**4** and **5**} (Acc=4-pyridyl), much better linear dependencies for each set are obtained (Fig. 2). This result proves that the anticipated dependencies are certainly plainly present if structural differences

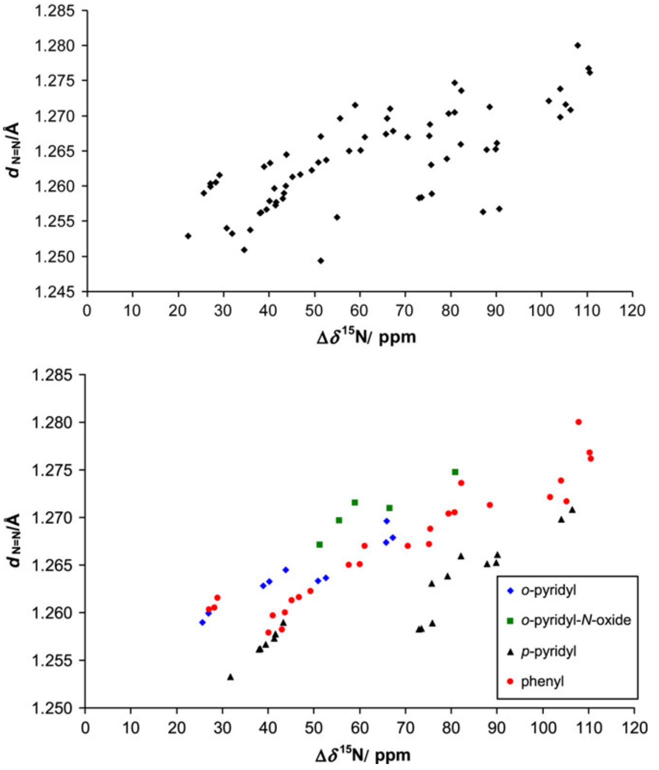


Figure 2. Correlations of the N═N bond length, $d_{N=N}$, vs the ^{15}N NMR chemical shift difference, $\Delta\delta_{15N}$, for all compounds **1**–**5** (top) and for the compounds subdivided into sets comprising of **1**, **2**, **3**, and (**4** and **5**) (bottom).

are not too proximate to the azo group and if only limited steric hindrance is present in the molecules. Clearly though, $\Delta\delta_{15N}$ is not the sought after sensitive, general parameter for quantitatively indicating the push–pull character in azobenzenes **1**–**5**.

Looking closer at the level of steric hindrance in **1**–**5**, based on the dihedral angles, Φ, present in the N═N–C$_i$–C$_o$ segments (Table 1 and supplementary data), whilst the donor side of the compounds is only slightly twisted from an ideal plane (maximum deviation observed, 3.62°), the acceptor side, contrastingly, can be twisted by up to 66° due to intense steric hindrance present in *ortho*,*ortho*-disubstituted cases. Cyano-disubstituted derivatives exhibit the slightest deviations (25–35°), followed by bromo-disubstituted derivatives (45–49°) with, finally, the strongest deviations shown in the case of *ortho*,*ortho*-diphenyl substitution (66°). The different spatial situation in the azobenzenes is evidently of influence on $\Delta\delta_{15N}$ because if the $\Delta\delta_{15N}$ vs $d_{N=N}$ correlations are examined with respect to unsubstituted, *ortho*-mono- and *ortho*,*ortho*-disubstituted compounds, different correlations, though with similar slopes, are obtained. Thus, the steric hindrance in the various groups of compounds can actually be quantified by $\Delta\delta_{15N}$ and $d_{N=N}$ by comparing the ordinate intercepts of the different correlations.

2.3. Occupation quotients, π*/π, and the *push–pull effect* in the azobenzenes 1–5

In Figure 3, the correlation of the calculated occupation quotient, π*/π, vs the calculated bond length, $d_{N=N}$, is portrayed with both values for the experimentally available compounds presented in Table 1 and for all compounds in Table S1 in the Supplementary data section. The correlation is highly linear (R^2=0.9727) and reveals that π*/π is the sought after ideal, sensitive and general parameter for evaluating the size of the *push–pull effect* in azobenzenes **1**–**5**. Neither structural differences (*ortho*-pyridyl, *ortho*-pyridyl-*N*-oxides, phenyl, and *para*-pyridyl) nor differences in steric hindrance due to *ortho*-mono- or *ortho*,*ortho*-disubstitution (vide supra) exert influence on the general dependency and the results are subject only to the Acc–π–Don properties of **1**–**5**.

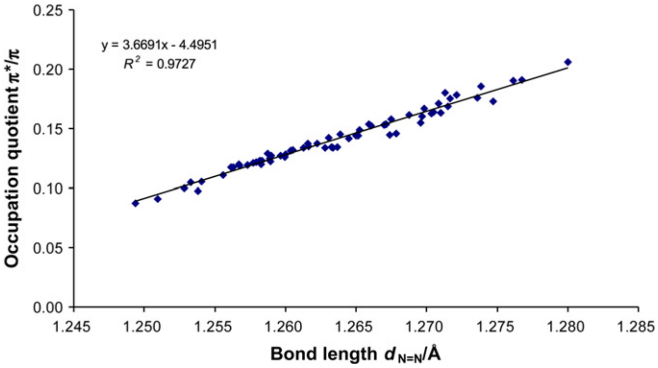


Figure 3. Correlation of the occupation quotient, π*/π, vs the bond length, $d_{N=N}$, of azobenzenes **1**–**5**.

2.4. Molecular hyperpolarizability, β_0, and the *push–pull effect* in substituted azobenzenes 1–5

Since a linear dependency between the push–pull character of Acc–π–Don chromophores and molecular hyperpolarizability, β_0, had been previously found,[27–29] azobenzenes **1**–**5** were similarly treated employing calculated occupation quotients, π*/π, and calculated β_0 values (β_0 values for the experimentally available compounds are presented in Table 1 and for all compounds in the Supplementary data section). The correlation of π*/π vs β_0 for all azobenzenes **1**–**5** is given in Figure 4. Though the dependency is uncustomarily poor, the tendency (i.e., increasing hyperpolarizabilities with rising push–pull character) is nevertheless present. However, it is far from the strong correlation anticipated based on previous studies of isophorone,[27] triazene,[28] and azine chromophores.[29] But, if the compounds are again subdivided as above into four sets comprising **1** (Acc=*ortho*-pyridyl), **2** (Acc=*ortho*-pyridyl-*N*-oxide), **3** (Acc=phenyl), and {**4** and **5**} (Acc=*para*-pyridyl), distinct correlations are more evident (cf. Fig. 4) which, though they remain somewhat erratic, are decidedly better than for all of the compounds **1**–**5** as a set. These dependencies can be further improved if differences in steric hindrance in the molecules are additionally considered. In Figure 4, the dependencies of the pyridyl compounds **1**, **2**, **4**, and **5** are subdivided based on the number of substituents in the *ortho* positions of the molecules. Three separate correlations are evident with steeply rising slopes for non- and *ortho*-monosubstituted acceptor moieties, and a much more gentle slope for the *ortho*,*ortho*-disubstituted analogues. Similar plots can also be obtained by subdivision of the substituted phenyl moieties in **3**.

Clearly steric strain due to *ortho*,*ortho*-disubstitution prevents free conjugation between the acceptor and donor moieties of the azobenzene derivatives. This reduces the proportionate gain of hyperpolarizability due to increasing push–pull character as for the unsubstituted or *ortho*-monosubstituted analogues whereby for these compounds, free conjugation along the Acc–π–Don chromophore allows for a proportionate increase in hyperpolarizabilty in concert with growing push–pull character. From these results, four generalities for the dependence of the hyperpolarizability on the *push–pull effect* in azobenzenes **1**–**5** can be drawn: (i) There is no general dependency of the hyperpolarizability of Acc–π–Don molecules with respect to the push–pull character present. (ii) When present in limited

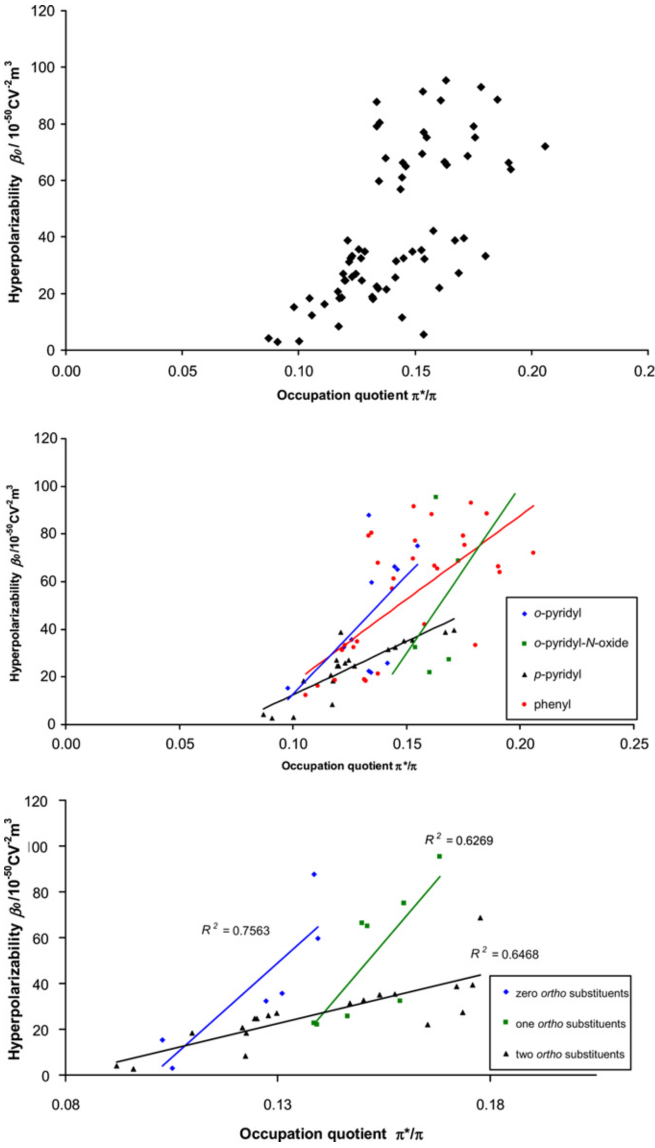


Figure 4. Correlations of molecular hyperpolarizability, β_0, vs occupation quotient, π^*/π, for all compounds **1**–**5** (top), for the compounds subdivided into sets comprising of **1**, **2**, **3**, and (**4** and **5**) (middle) and for the pyridyl derivatives **1**, **2**, **4**, and **5** only (bottom) subdivided based on the presence of none, one or two *ortho* substituents in the acceptor moiety.

circumstances, any dependency relates to both the acceptor and donor moieties of the Acc–π–Don compounds. (iii) Differences in steric hindrance precluding free conjugation along the Acc–π–Don chromophore have to be considered. Only if aromatics/heteroaromatics groups at the N═N bond with comparable steric strain is considered with respect to substituent influences on both hyperpolarizability and push–pull character can strictly linear dependences be attained. (iv) With free conjugation along the chromophore, the increase in push–pull character due to substituent effects is attended by a greater increase in hyperpolarizability. Since the results here conflict with previous results for the $(Acc)_2C{=}N{-}N{=}C(Don)_2$ chromophore,[29] it must therefore be a result of the peculiar properties of azobenzene derivatives.

Assuming the above results and related previous studies[27–29] hold, it can be reliably concluded that the effects of substituents on various Acc–π–Don chromophores are determinate of the hyperpolarizability in certain compounds; certainly it can be neither the according change in the push–pull character of the Acc–π–Don compounds nor the amount of present steric hindrance present in the chromophore. Even if this study reports the opposite, push–pull-substituents for strongly sterically hindered chromophores can still greatly increase molecular hyperpolarizability with only a minor change of push–pull properties.[29]

2.5. Potential application of azobenzenes 1–5 as NLO materials

Finally, the molecular hyperpolarizabilities, β_0, of azobenzenes **1**–**5** have been evaluated with respect to their potential use as NLO materials. With regards to sets of compounds, the largest β_0 values were found for the *ortho*-pyridyl-*N*-oxides **2**, followed by the phenyl compounds **3**, then the *ortho*-pyridyl derivatives **1**, and then finally the *para*-pyridyl azobenzene derivatives **4** and **5**.

$$\beta_0 : N-\text{oxides}(\mathbf{2}) > \text{phenyl}(\mathbf{3}) > ortho-\text{pyridyl}(\mathbf{1}) > para-\text{pyridyl}(\mathbf{4},\mathbf{5}).$$

Of note, large hyperpolarizabilities were obtained only if both a nitro group in the acceptor part and a $N(CH_2CH_2OH)_2$ group in the donor part were present. If just one of the groups is lacking, the value of β_0 drops notably; with both groups are not present, the smallest β_0 values throughout the whole series were obtained. +M-substituents at the donor moieties such as *O*-alkyl and +I substituents as methyl should support the donor activity of these molecules. It can be ascertained that *meta*-substitution strengthens donor character and accordingly the value of β_0, whilst *ortho*-substitution, due to steric hindrance, reduces the value of β_0. In the acceptor part of **1**–**5**, the effects of *para*-, *ortho*-mono-, and *ortho*,*ortho*-disubstitution were examined whereby it is demonstrated that a bromo substituent instead of a nitro substituent in the *para*-position, due to +M character, reduces the value of β_0 accordingly and thereby corroborating the strong effect of the nitro group as an acceptor substituent. The presence of *ortho*-mono- or *ortho*,*ortho*-disubstitution by cyano groups increase the value of β_0, though the increase in the case of *ortho*, *ortho*-disubstitution compared with *ortho*-monosubstitution is mitigated by the effect of steric hindrance (evaluated based on the magnitude of the perturbation of the dihedral angle, Φ, of the $N{=}N{-}C_i{-}C_o$ segment). For example:

	3a (*o*,*o*-di-C≡N)	**3e** (*o*-C≡N)	**3i** (unsubstituted)
β_0:	79.2	77.0	67.9
Φ:	7°	1.5°	0.5°

In the *para*-pyridyl derivatives **4**, the nitro group is not present and hyperpolarizabilities are decisively lower. Interestingly, in *ortho*,*ortho*-disubstituted derivatives, the consequent steric hindrance still has an effect, though its effects are somewhat dampened even if it appears to be strongly based on the perturbation of Φ, which can be up to 48°. For example:

	4d (*o*,*o*-di-Ph)	**4h** (*o*,*o*-di-Br)	**4i** (*o*,*o*-di-C≡N)	**4l** (*o*,*o*-C≡N,Br)	**4k** (*o*,*o*-C≡N,Ph)
β_0:	20.8	26.0	39.5	35.4	32.5
Φ:	45°	48°	2.5°	27°	25°

Of the azobenzene derivatives **1**–**5**, which are experimentally available,[30] **2a** and **3d** are the compounds, which should be most useful for NLO applications since they possess the largest β_0 values, 95.5 and 93.0, respectively, and have only slight deviations for the dihedral angles of the $N{=}N{-}C_i{-}C_o$ segments, another necessary requirement for application as NLO materials:

$$\mathbf{2a}\Big(X = N\rightarrow O,\ Y = NO_2,\ R^1 = OC_8H_{17},$$
$$R^2 = N(CH_2CH_2OH)_2:\ ß_0 = 95.5\Big(\sphericalangle:\ 1.3°\text{to } 3.5°\Big)$$

$$\mathbf{3d}\Big(X, R = C\equiv N,\ Y = NO_2,\ R^1 = OC_8H_{17},$$
$$R^2 = N(CH_2CH_2OH)_2:\ ß_0 = 93.0\Big(\sphericalangle:\ 1.2°\text{to } 1.4°\Big)$$

Besides nitro and $N(CH_2CH_2OH)_2$ groups conveying the Acc–π–Don property to the azobenzene chromophore, obviously flat molecules for free π-electron conjugation, *meta*-alkoxy (as an additional donor group) and *ortho*-N→O substitution (as an additional acceptor moiety) enforce this activity and approve these two derivatives from the variety **1**–**5** studied, especially for the application as NLO materials. Of the additionally computed analogues (cf. Table in the Supplementary data), no other compounds possessing larger hyperpolarizabilities were found.

3. Conclusions

^{15}N NMR chemical shift differences, $\Delta\delta_{15N}$, have been experimentally measured employing HMBC experiments and also calculated at the DFT level of theory for comparison of the changes in the occupation quotients, π^*/π, and the bond lengths, $d_{N=N}$, of the N=N partial double bond obtained by theoretical calculations at the same level of theory. Whilst $\Delta\delta_{15N}$ was found not to be a sensitive and general indicator of the push–pull character of azobenzenes **1**–**5**, an excellent linear correlation of π^*/π vs $d_{N=N}$ was obtained, thus proving the occupation quotient to be an ideal, sensitive and general parameter for the size of the *push–pull effect* in the present group of compounds. Neither structural differences (*ortho*-pyridyl, *ortho*-pyridyl-*N*-oxides, phenyl, and *para*-pyridyl) nor different levels of steric hindrance exert influence on the general dependence and the effects are subject only to the Acc–π–Don properties of **1**–**5**. Molecular hyperpolarizabilities, β_0, of the Acc–π–Don chromophore, also computed for **1**–**5**, are dependent, in addition to the push–pull character, on the structure and substitution of both acceptor and donor moieties and the steric hindrance present within the chromophore. The most promising azobenzenes **1**–**5** for potential NLO applications are able to be inferred from this analytical approach.

4. Experimental

4.1. NMR measurements

The NMR spectra of the experimentally available azobenzene derivatives **1**–**5** were recorded as 1D and 2D experiments at 600/500 and 60.8/50.7 MHz, accordingly, for ^{1}H and ^{15}N, respectively, at room temperature in acetone-d_6 or CD_2Cl_2. ^{1}H NMR spectra were referenced internally to TMS (δ=0 ppm). Indirect measurement of δ_{15N} was performed using gradient-selected HMBC and δ_{15N} were referenced externally using nitromethane as reference (80%, δ=0 ppm). 2D acquisition parameters: number of scans, 64–128; sweep width, 10 ppm for ^{1}H and 250 ppm for ^{15}N. 2D processing parameters: zero filling in f_2 and f_1; window function, π/3-shifted squared sine bell in f_2 and f_1; f_2 processed in magnitude mode.

4.2. Computational details

Natural Bond Orbital (NBO) population analyses[35] were performed for DFT geometry-optimized structures at the B3LYP/6-311G** level of theory without constraints[36] using Gaussian 03.[37] Molecular hyperpolarizabilities, β_0, at zero frequency were calculated using the same model chemistry and the default parameters provided by the Gaussian keyword 'polar=enonly'. 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 NMR chemical shifts, δ_{15N}, were calculated using the GIAO method[34] by DFT at the B3LYP/6-311G** level of theory without inclusion of the solvent and referenced to nitromethane calculated at the same level. All calculations were carried out on SGI workstations and LINUX clusters.

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Supplementary data

^{15}N chemical shifts, bond lengths, steric hindrance, occupation quotient, and molecular hyperpolarizabilities of all azobenzene derivatives **1**–**5** can be found as supplementary data in the online version, at doi:10.1016/j.tet.2010.04.067.

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