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Chemistry and Nonlinear Optical Properties of New 2H-Benzotriazole Derivatives

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Abstract: The 2H-benzotriazolyl group is introduced as a new electron-withdrawing group for NLO-active chromophores. Novel benzotriazole derivatives and hydrazones have been synthesized. While their electronic structure and acceptor capability is comparable to those of structurally related nitro compounds, 2H-benzotriazoles show a more favorable transparency-nonlinearity trade-off for NLO applications. The first molecular hyperpolarizabilities β have been measured with hyper-Raleigh scattering (HRS). Copyright © 1996 Elsevier Science Ltd

Introduction

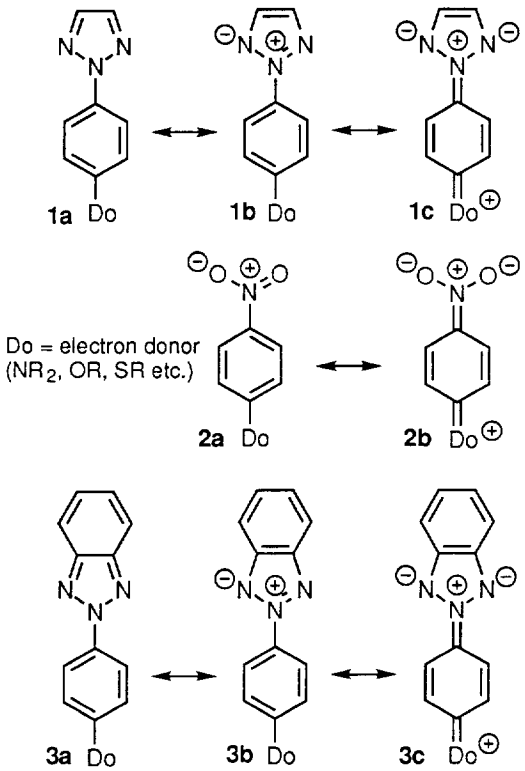
The development of materials with special optical,[1] magnetic[2] and electrical[3] properties that are suitable for molecular electronics[4] has become one of the important objects in organic and inorganic synthesis within the last years. In this paper we introduce the benzotriazole group as a new acceptor group for organic charge-transfer systems. The 2H-benzotriazolyl group mimics the electronic properties of the nitro group. The relationship between these two groups is reflected by UV/VIS and NMR spectroscopic data as well as by the chemical reactivity of 2H-benzotriazolyl and nitro substituted π-electron systems. It is interesting to compare the first hyperpolarizabilties β of charge-transfer systems containing these two types of acceptor groups. A possible application of 2H-benzotriazolyl substituted charge-transfer systems is their implementation in nonlinear optical devices for e. g. frequency doubling (second harmonic generation, SHG). One of the serious problems of organic frequency doublers is the need for an optical window at the frequency of the second harmonic (i. e., at 415 nm for common 830 nm infrared diode lasers) to avoid reabsorption of the generated frequency doubled light. The extensive work of Cheng[5] has shown that there is a *transparency-nonlinearity trade-off* for standard charge-transfer compounds. One advantage of the benzotriazole group can be the shorter absorption wavelength at the same range of β values as observed with the corresponding nitro compounds. For macroscopic bulk systems such as guest-host systems the solubility of the chromophores plays an important role. High loading of the NLO dye is necessary to achieve high $\chi^{(2)}$ values. As compared to dipolar nitro compounds which tend to have rather low solubilities the corresponding benzotriazole derivatives exhibit relatively good solubilities in solvents commonly used solvents used for the spin coating process.

Results

Electron-withdrawing properties of the 2H-1,2,3-triazolyl group

The role of benzotriazoles in organic synthesis has been thoroughly studied[6] and there are many applications of *N*-substituted benzotriazoles (cf.[7-9]). As regards nonlinear optical properties, only the 2H-1,2,3-triazolyl group in 2-(4'-nitrophenyl)-2H-1,2,3-triazole has been mentioned as an electron *donor* in connection with other azole derivatives.[10]

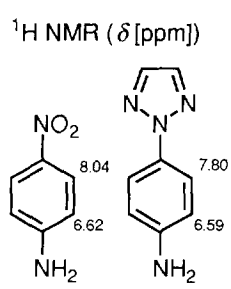
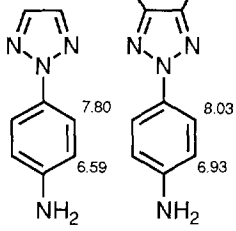
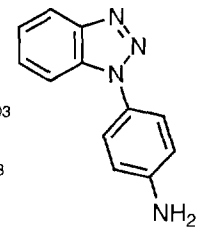
1,2,3-Triazoles and benzotriazoles are electron-poor heterocycles. 2H-1,2,3-triazole derivatives **1** and the corresponding 2H-benzotriazole derivatives **3** are electronically related to nitro compounds **2**. With 1-triazolyl compounds this relationship is less pronounced. In contrast to the



electron-withdrawing 2-triazolyl group the 1-triazolyl group is expected to behave as a (weak) electron-releasing group. Resonance structure **3a** is *ortho* quinoid and resonance structures **3b** and **3c** should therefore be favoured in the ground state. Thus, the electron-withdrawing properties of the 2H-benzotriazolyl group are expected to be stronger than those of the 2H-1,2,3-triazolyl group. This is born out by the similarity of the NMR data of *p*-nitroaniline (PNA) **4**, 2-(4-aminophenyl)-2H-1,2,3-triazole **5** and 2-(4-aminophenyl)-2H-benzotriazole **6** as well as the Hammett σ_p constant of the 2H-benzotriazolyl group ($\sigma_p = 0.51$, $\sigma^-_p = 0.57$)[11] (cf. table 1). Accordingly, the electronic spectra show (cf. table 1) that **6**[12] absorbs at longer wavelengths than 1-(4-aminophenyl)-1H-benzotriazole **7**.[13] By virtue of its more extended π-electron system **6** also absorbs at

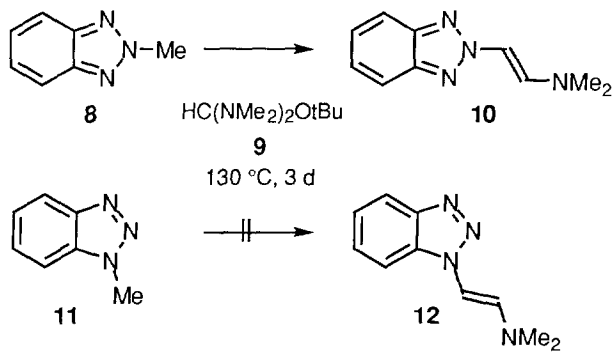
longer wavelenghts than **5**.[14] The absorption maxima of **5** - **7** are found at considerably shorter wavelenghts than the maximum of **4**[15] which is exactly the effect necessary for SHG of diode lasers.

Table 1. ^{1}H NMR data (δ [ppm]) and UV/Vis spectra (λ_{max} [nm]) of *p*-nitroaniline **4**, 2-(4-aminophenyl)-2H-1,2,3-triazole **5**, 2-(4-aminophenyl)-2H-benzotriazole **6**, and 1-(4-aminophenyl)-1H-benzotriazole **7**

^{1}H NMR (δ [ppm])			
			
4	**5**	**6**	**7**
λ_{max} [nm] (EtOH)			
373	290	344	304

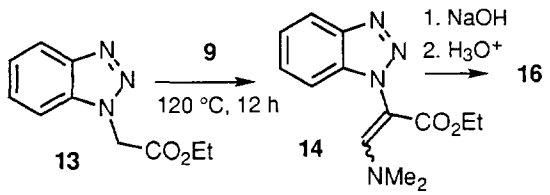
2-Methylbenzotriazole as an active methylene compound

If the 2H-benzotriazolyl group has indeed the electron-withdrawing properties described above 2-methylbenzotriazole is expected to behave as an active methylene compound. 1-Methylbenzotriazole **11** and 2-methylbenzotriazole **8** can be prepared by thermal decarboxylation of the corresponding benzotriazolylacetic acids.[16] Heating of **8** with Bredereck's reagent **9** gives rise to the enamine **10**. The reaction of **9** with **8** is, however, much more sluggish than that with nitromethane. Obviously, the 2H-benzotriazolyl group is less effective than the nitro group in activating a methylene group. **11** did not react with **9** under comparable conditions.



The enamine **10** shows a strong solvatochromism which indicates that this compound may display nonlinear optical activity[17] (UV/VIS: λ_{max} (lg ε) = 353 nm (4.392), in Et_2O; 362 nm (4.424), in MeCN; 364 nm (4.402), in EtOH; $\Delta\tilde{\nu}$ (Et_2O/MeCN) = 704 cm^{-1}; $\Delta\tilde{\nu}$ (Et_2O/EtOH) = 856 cm^{-1}). Like some other 2H-benzotriazole derivatives[12] **10** displays in toluene an intense blue, in the solid state a green-blue fluorescence.

In order to obtain **12** ethyl 1-benzotriazolylacetate[18] **13** was heated with **9** to produce **14**, the hydrolysis of which, however, gave rise to 1-benzotriazolylacetic acid **16** instead of **12**.



Benzotriazolylvinamidinium salts and benzotriazolylpyrimidines

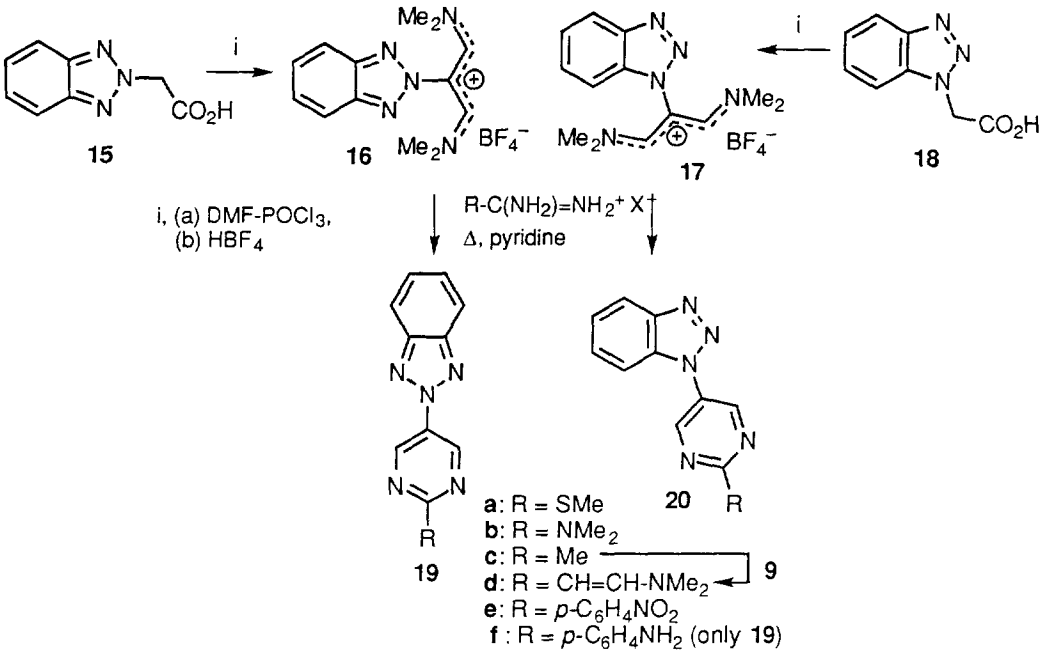
With respect to materials for nonlinear optics (NLO) that are transparent above 400 nm (λ_{max} <400 nm, $\lambda_{cut\text{-}off} \leq 415$ nm) it is important to realize that pyridine and pyrimidine derivatives absorb at shorter wavelenghts (ca. 50 and 100 nm, resp.)[19] than the corresponding isocyclic compounds (π-π^*). As 2,5-disubstituted pyrimidines can be prepared from vinamidinium salts and amidines[20] our plan was to synthesize donor-acceptor substituted pyrimidines (structure **3** with a pyrimidine instead of a benzene ring) with the 2H-benzotriazolyl group as electron acceptor using 2-(2H-benzotriazolyl)-vinamidinium tetrafluoroborate **16** as starting material. Pyrimidines derived from 2-(1H-benzotriazolyl)-vinamidinium tetrafluoroborate **17** could be used as the corresponding donor substituted derivatives. After our experiments had been concluded[21] the synthesis of **17**, ClO_4^- and PF_6^- instead of BF_4^-, was reported.[22]

2H-Benzotriazolylacetic acid **15** and 1H-benzotriazolylacetic acid **18** react with dimethylformamide-phosphorus oxychloride (cf.[20b,22]) and work-up with tetrafluoroboric acid to form the vinamidinium salts **16** and **17**. The IR, ^1H NMR and UV/VIS spectra of **16** and **17** are closely related. In the ^1H NMR spectra two signals of the protons of the dimethylamino groups are observed (**16**: δ = 2.05, 3.38; **17**: δ = 2.03, 3.34) which indicates hindered rotation of the iminium groups.

16 and **17** can be condensed with amidinium salts in boiling pyridine to provide the pyrimidine derivatives **19a-c** and **20a-c** (cf.[22]). When heated with **9**, **19c** and **20c** give rise to the enamines **19d** and **20d**, respectively.

The pyrimidinyl-1H-benzotriazoles **20a,b** absorb at shorter wavelengths than their 2-isomers **19a,b** in accordance with the donor-acceptor pattern of **19a,b**. Both types of compounds are not solvatochromic. The absorption maximum of **19b** (λ_{max} = 337 nm in toluene or DMSO) is found at shorter wavelengths than that of 2-(4-dimethylaminophenyl)-2H-benzotriazole (**6**, NMe_2 instead of NH_2: λ_{max} = 354 nm, in Et_2O; 359 nm, in EtOH).[12]

Further evidence for the electron-withdrawing properties of the 2H-benzotriazolyl group comes from the ^1H NMR spectra of **19d** and **20d**. The spectrum of **19d** shows the singlet of the pyrimidine protons more than 0.5 ppm downfield as compared with that of **20d**.



19d and **20d** are solvatochromic, in contrast to **19a,b** and **20a,b** (**19d**: UV/VIS: λ_{max} (lg ε) = 396 nm (4.649), in toluene, 404 nm (4.627), in DMSO; $\Delta\tilde{\nu}$ (toluene/DMSO) = 500 cm^{-1}. – **20d**: (UV/ Vis: λ_{max} (lg ε) = 352 nm (4.470), in toluene; 357 nm (4.484), in DMSO; $\Delta\tilde{\nu}$ (toluene/DMSO) = 398 cm^{-1}). **19d** is stronger solvatochromic than **20d** which is in accord with the higher polarity of **19d** as a consequence of the electron-withdrawing effect of the 2H-benzotriazolyl group.

The pyrimidines **19a-d** and **20d** show blue fluorescence in toluene solution and blue (**19a,b**) and yellow (**19d, 20d**) fluorescence in the solid state.

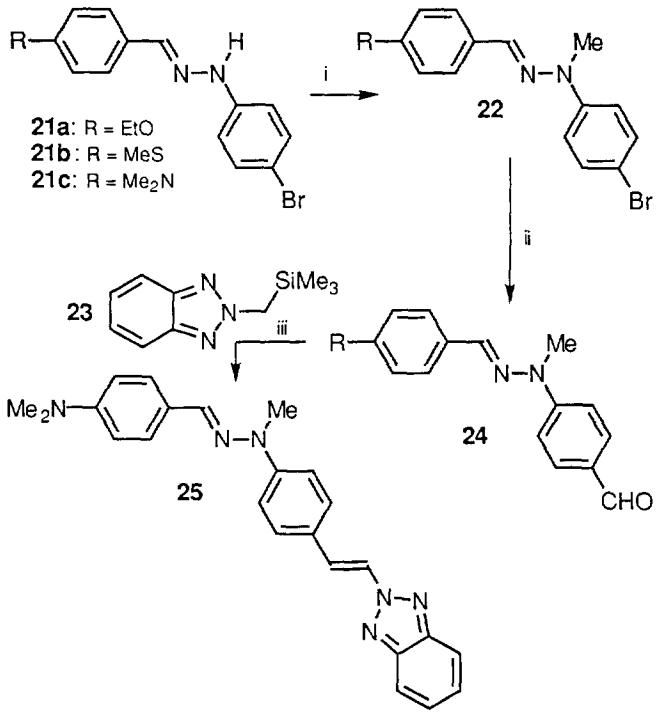
In donor-acceptor substituted biphenyl derivatives the resonance interaction between the donor and acceptor groups is diminished because the phenyl rings are not coplanar (cf.[23,24]). This could give rise to a hypsochromic shift of the UV/VIS absorption as compared with that of donor-acceptor substituted benzene derivatives (cf. **4**). A high hyperpolarizability β might be, however, retained by virtue of the extended π-electron system. Thus, donor-acceptor substituted biphenyl derivatives and diazabiphenyl systems derived from **19** might be interesting for NLO (cf.[23]), especially with respect to the *transparency-nonlinearity trade-off*.

The diazabiphenyl derivatives **19e,f** and **20e** can be obtained by reacting **16** and **17** with benzamidines. The very low solubility of **19e,f** makes it difficult to study their spectroscopic and NLO properties. ^1H NMR spectra could be measured in trifluoroacetic acid solutions, UV/VIS spectra in DMSO solutions.

The donor-acceptor substituted compound **19f** (λ_{max} = 434 nm) absorbs at longer wavelengths than the acceptor-acceptor substituted derivative **19e** (λ_{max} = 342 nm). **19f** also absorbs at longer wavelengths than **19b** (λ_{max} = 337 nm). Thus, if diazabiphenyl derivatives such as **19f** are twisted this twisting is not sufficient to give rise to $\lambda_{max} \leq 400$ nm.

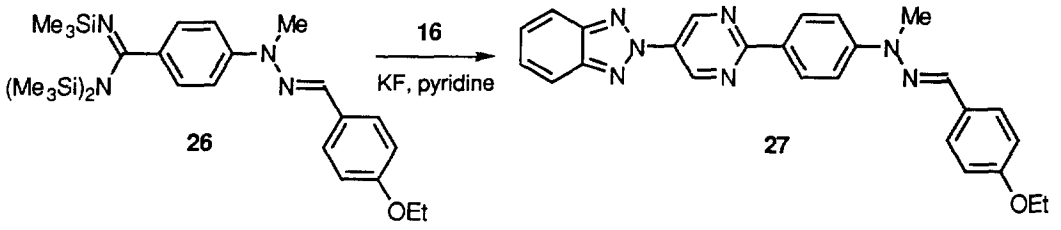
Benzotriazolyl-arylhydrazones

Arylhydrazones show high hyperpolarizabilities and nonlinear optical susceptibilities $\chi^{(2)}$.[25] Therefore we tried to combine the NLO properties of **19** with those of arylhydrazones. To this end the bromohydrazones **22**, prepared by methylation of **21**, were lithiated and the lithium derivatives reacted with *N*-methylformanilide to form the aldehydes **24**. Condensation of **24c** with 2-trimethylsilylmethyl-2H-benzotriazole **23**[6,26] under Peterson conditions[27] gives rise to the 2H-benzotriazolylvinylphenylhydrazone **25** in which two donor-acceptor moieties are combined, their partial dipole moments pointing in the same direction. The one moiety consists of *p*-amino-β-(2H-benzotriazolyl)-styrene, the other one of *p*-dimethylaminobenzaldehyde imine. **25** is closely related to donor-acceptor substituted styrenes such as *p*-dimethylamino-β-nitrostyrene for which a hyperpolarizability $\beta = 50 \times 10^{-30}$ esu has been calculated.[24a]



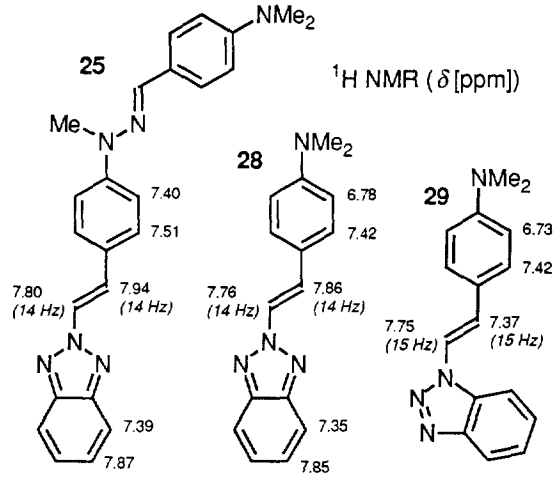
Reagents and conditions: i, (a) BuLi, THF, -78 °C, (b) MeI; ii, (a) tBuLi (2 equiv.), THF, -78 °C, (b) PhN(Me)CHO, -78 °C → room temp., (c) H_3O^+; iii, (a) **23**, BuLi, –78 °C, (b) NH_4Cl-H_2O

Another pathway to benzotriazolylarylhydrazones is the reaction of the per(trimethylsilyl)amidine **26**, prepared from the corresponding nitrile using standard conditions,[28] with **16** to form the pyrimidine derivative **27** (the synthesis of pyrimidine from per(trimethylsilyl)amidines and vinamidinium salts gives much higher yields than that with amidines[29]).



The ^{1}H NMR spectrum of **27** could be measured only in trifluoroacetic acid and can therefore hardly be compared with the spectra of other triazole derivatives. Table 2 shows selected ^{1}H NMR data of **25**, **28**[30] and **29**.[27] The coupling constants of the vinyl proton signals are in accord with a *trans* arrangement of the substituents at the C=C bonds.

Table 2. UV/Vis (λ_{max} [nm]) and selected ^{1}H NMR data (δ [ppm]) of some benzotriazole derivatives



UV/Vis (λ_{max} [nm])

in toluene:	417	in Et_2O:	384
in DMSO:	427	in MeCN:	390

$\Delta\tilde{\nu}$ (toluene/DMSO)	$\Delta\tilde{\nu}$ (Et_2O/MeCN)
562 cm^{-1}	401 cm^{-1}

Compound **25** is solvatochromic (cf. table 2); its λ_{max} is red-shifted by roughly 35 nm as compared with that of **28** as a consequence of the replacement of the dimethylamino group by the benzylidene hydrazone group. The pyrimidine derivative **27** (UV/VIS: λ_{max} = 416 nm, in toluene; λ_{max} = 419 nm, in DMSO; $\Delta\tilde{\nu}$ (toluene/DMSO) = 172 cm^{-1}) shows only a weak solvatochromism.

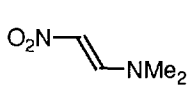
Results and discussion of HRS measurements

Table 3 contains experimentally determined first hyperpolarizabilities β and UV/VIS data of compounds **2**, R = NMe_2, **3** R = NMe_2, **4**, **10**, **19d**, **30** and **31**. The HRS measurements were carried out in chloroform versus **4** (PNA)/chloroform as an external reference. The spectra also were taken using chloroform as a solvent.

Table 3. β-Values as determined by hyper-Raleigh scattering at 1064 nm and spectroscopic data of the investigated compounds in chloroform as solvent

compound	λ_{max} [nm]	β [10^{-30} esu]
2, Do = NMe_2,	391	25
3, Do = NMe_2,	362	26
4 (PNA)	348	17
10	363	19
19d	395	81
30	348	8[a]
31	438	98[b]

[a] L. T. Cheng, unpublished results (extrapolated to 1064 nm via the two-level model)
[b] From reference [5], extrapolated to 1064 nm via the two-level model



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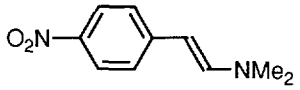

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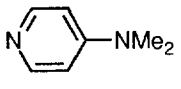

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With regard to NLO applications the measurements reflect a highly interesting relationship between the nitro group on the one hand and the benztriazolyl group on the other hand. In charge-transfer compounds the nitro group as an electron acceptor gives rise to high β-values but also to strong bathochromic shifts. The benztriazolyl group, however, induces for the same range of β-values a much less bathochromic shift as the hyperpolarizabilities of compounds **2** ([Do = NMe_2) and **3** (Do = NMe_2) show. The β-values are almost identical while **3** is absorbing at about 30 nm shorter wavelengths than **2**. The same tendency can be found by comparing **10** and 1-dimethylamino-2-nitroethylene **30**, both compounds having shorter π-electron systems than **2** and **3**. **10** is absorbing only at slightly longer wavelengths than **30**, but the β value of **10** is more than twice that of **30**. These two pairs – **2/3** and **10/30** – demonstrate that donor -acceptor substituted π-electron systems containing the benzotriazolyl group may be better candidates for NLO applications than the corresponding nitro derivatives.

It is well known that many donor-acceptor substituted aromatics containing nitro groups as acceptors have a rather low solubility. This is not the case with the benzotriazole derivatives in-

vestigated here. Since large $\chi^{(2)}$ values from bulk materials can only be obtained with high concentrations of the embedded chromophores, solubility is an important factor in NLO applications. Although the benzotriazoles have a less favourable nonlinearity / mass ratio than the corresponding nitro compounds the better solubility of the former may compensate for this drawback.

A further interesting comparison can be made between **3** (Do = NMe_2), **10**, **19d** and **31**. The replacement of the phenyl ring of **3** (Do = NMe_2) with an ethylene group (→ **10**) does not change the absorption maximum, it reduces, however, the β value. This may be a consequence of the smaller conjugated π-electron system of **10** which reduces the polarizability of this compound. The comparison of **3** (Do = NMe_2) with **19d** which contains an additional ethylene group (and a pyrimidine ring instead of a benzene ring), and of **10** with **19d** shows that a threefold to fourfold increase in β goes along with only a moderate increase in λ_{max}. Although the contribution of the pyrimidine ring of **19d** to the hyperpolarizability is not quite clear (the nitrogen atoms are electron withdrawing and thus are supposed to amplify the electron acceptor effect of the benzotriazolyl group (cf.[31]) the series **10**, **3** (Do = NMe_2), and **19d** reflects the well established rule that a larger π-electron system gives rise to an increase in β. On condition that the contribution of a pyrimidine ring to β is similar to that of a phenyl ring the comparison of **19d** with **31** indicates once more that the replacement of a nitro group with a benzotriazolyl group gives a more favourable transparency-nonlinearity trade-off.

In this context it interesting to note that 4-dimethylaminopyridine **32** with λ_{max} = 259 nm exhibits a first hyperpolarizability ($\beta = 19 \times 10^{-30}$ esu) which is even slightly higher than that of the electronically closely related PNA **4** with λ_{max} = 348 nm. Thus, this might be a further possibility to replace the nitro group in donor-acceptor π-electron systems in order to attain dipolar compounds with both λ_{max} < 400 nm and high β values for SHG.

In summary, these observations emphasize the interesting properties of the 2H-benzotriazolyl group for NLO applications.

Experimental

Determination of the hyperpolarizability via hyper-Rayleigh scattering (HRS)

The basics of hyper-Rayleigh scattering are described in detail.[32] To make the understanding for the reader easier, the most important points are shortly repeated, and our slighty modified evaluation of the data is explained.

The second harmonic intensity $I(2\omega)$ is a function of the fundamental intensity I_0. Variation of the fundamental intensity, obtained by rotating a half wave plate (rotating angle ϕ, deviation angle α) between two polarizers, leads to the fit formula (1).

$$I(2\omega) = a \cdot [\sin(2\phi + \alpha)]^4 + b \qquad (1)$$

where

$$a = G \cdot B^2 \cdot I_0^2 \qquad (2)$$

and

$$B^2 = \underbrace{N_g \cdot \beta_g^2}_{solute} + \underbrace{N_l \cdot \beta_l^2}_{solvent} \qquad (3)$$

G is a geometrical factor, N the number density and b an intensity offset. Measurements at different number densities of the solute show a linear dependence of the fit parameter a on N_g. From the intercept c and the slope m, β_g can be calculated when β_I is known (4a) or vice versa (4b) (*internal reference method*).

$$|\beta_g| = \sqrt{\frac{m \cdot N_I}{c}} \cdot |\beta_I| \quad (4a) \qquad |\beta_I| = \sqrt{\frac{c}{m \cdot N_I}} \cdot |\beta_g| \quad (4b)$$

It is also possible to correlate the slope of the substance to be measured with the slope of *p*-nitroaniline (PNA) (of which the β value is well known[33]) in the same solvent (*external reference method*, (5)).

$$\beta = \sqrt{\frac{m}{m_{PNA}}} \cdot \beta_{PNA} \quad (5)$$

Figures 1 and 2 show typical HRS curves on the basis of compound **19d** which yields a hyperpolarizability of $\beta = 81 \times 10^{-30}$ esu in chloroform.

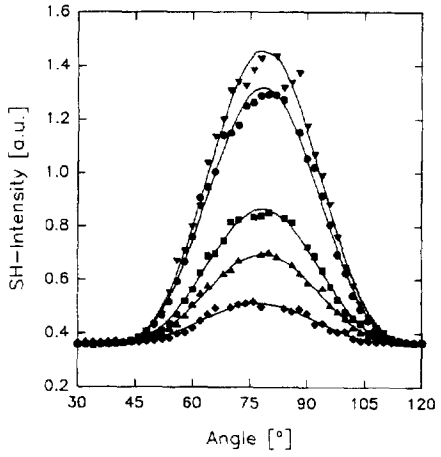

Figure 1. The intensity of the frequency doubled light as a function of the rotating angle φ for 5 different concentrations (number densities) of **19d** in chloroform. The rotation of the angle φ corresponds to an increase and a decrease of the light intensity I_0 of the fundamental laser beam. The experimental data were fitted with equation (1).

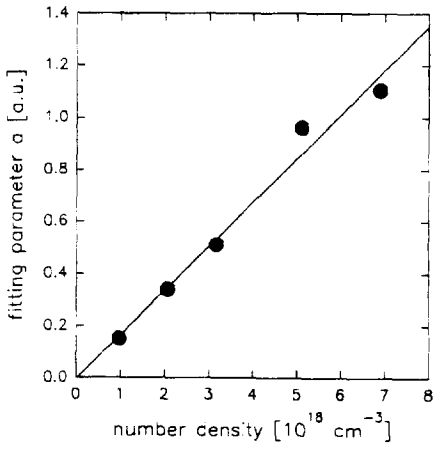

Figure 2. A plot of the parameter a as a function of the number density of **19d** in chloroform. From the slope m of the β value of **19d** can be obtained with equation (5) and the corresponding β value of the external reference **4** (PNA).

Experimental setup

Figure 3 shows the setup for the experimental determination of the first hyperpolarizability β via the HRS-technique. In contrast to the setup of Clays and Persoons[34] the beam is not focused into the sample cell but reduced before to a diameter of 1.5 mm with the help of a telescope. This prevents problems with dielectrical breakdowns within the sample. The front and rear windows of the sample cell are shielded to prevent signal contributions from the glass walls, especially from adsorbed dye molecules. Because of the large effective cathode diameter of the Thorn-EMI 9635QA there is no need for focusing the second harmonic scattered light into the photomultiplier, which makes the adjustment much less complicated. The measurements were carried out at a fundamental wavelength of 1064 nm.

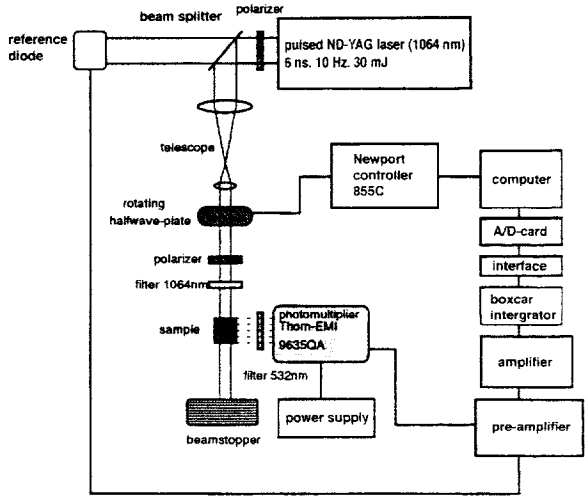

Figure 3. Experimental setup of the HRS experiment

Experimental Procedures

^{1}H NMR spectra were obtained with Bruker WP 80 (80 MHz), Varian VXR 400 S (400 MHz), ^{13}C NMR spectra with Varian VXR 400 S (100.22 MHz) spectrometers. IR spectra were recorded on Perkin-Elmer 125 and Bruker IFS 45 spectrometers, UV/VIS spectra on Zeiss DMR 10 and Perkin-Elmer Lambda 3 spectrometers. Mass spectra were determined on a Finnigan MAT 90 spectrometer.

2-(2-Dimethylaminoethenyl)-2H-benzotriazole (**10**): A mixture of 2-methyl-2H-benzotriazole (0.53 g, 3.98 mmol) and *tert*-butyloxy-bis-dimethylamino-methane **9** (1.60 ml,7.75 mmol) was stirred at 130 °C for 3 d. Ethanol was added to the product and the remaining yellow crystals collected by filtration and washed with methanol and pentane. Yield 0.18 g (24%), yellow crystals, M.p. 98-99 °C. IR (KBr): $\tilde{\nu}$ = 1662 cm^{-1}, 1382, 1284, 1109, 944, 758, 747, 711. UV/VIS (Et_2O): λ_{max} (lg ε) = 258 nm (3.795), 264 (3.817), 290 (sh, 3.670), 353 (4.392); (MeCN): λ_{max} (lg ε) = 259 nm (3.764), 265 (3.776), 362 (4.408); (EtOH): λ_{max} (lg ε) = 259 nm (3.715), 265 (3.671), 290 (3.663), 364 (4.402). ^{1}H NMR ($CDCl_3$): δ = 2.80 (s, 6 H, $N(CH_3)_2$), 6.57 (d, J = 12 Hz, 1 H, C<u>H</u>=CH-NMe_2), 7.27 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 2 H, 4-H, 7-H), 7.70 (d, J = 12 Hz, 1 H, CH=C<u>H</u>-NMe_2), 7.76 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 2 H, 5-H, 6-H). ^{13}C NMR ($CDCl_3$): δ = 40.67 (NMe_2), 102.46 (<u>C</u>H=CH-

NMe_2), 116.60 (C-4, C-7), 125.21 (C-5, C-6), 138.46 (CH=CH-NMe_2), 143.88 (C-3a, C-7a). MS (70 eV), *m/z* (%): 189 (12) [M^+ + 1], 188 (100) [M^+], 119 (51), 83 (27), 69 (21), 42 (30). Anal. Calcd. for $C_{10}H_{12}N_4$ (188.2): C 63.81; H 6.43; N 29.77. Found: C 63.51; H 6.30; N 29.67.

Ethyl 1-(1H-benzotriazol-1-yl)-2-dimethylamino-acrylate (14): A mixture of ethyl 1H-benzotriazol-1-yl-acetate (1.00 g, 4.87 mmol), *tert*-butyloxy-bis-dimethylamino-methane **9** (1.10 ml, 5.33 mmol) and *N,N*-dimethylformamide (DMF) (10 ml) was stirred for 12 h at 120 °C. Volatile products were distilled off in vacuo and the residue recrystallized from 200 ml of high-boiling petrol ether. Yield 0.71 g (56%), colorless crystals, m.p. 87-88 °C. IR (KBr): $\tilde{\nu}$ = 1690 cm^{-1}, 1622, 1610, 1303, 1222, 1099, 1069. UV/VIS (Et_2O): λ_{max} (lg ε) = 271 nm (4.377); (EtOH): λ_{max} (lg ε) = 273 nm (4.464). ^1H NMR ($CDCl_3$): δ = 1.07 (t, J = 7 Hz, 3 H, CH_2CH_3), 2.57 (br. s, 6 H, $N(CH_3)_2$), 4.05 (q, J = 7 Hz, 2 H, CH_2CH_3), 7.25-7.47 (m, 3 H, benzotriazolyl-H), 7.78 (s, 1 H, CH-NMe_2), 7.93-8.10 (m, 1 H, benzotriazolyl-H). MS (70 eV), *m/z* (%): 260 (1) [M^+], 203 (100), 42 (29). Anal. Calcd. for $C_{13}H_{16}N_4O_2$ (260.3): C 59.99; H 6.20; N 21.52. Found C 60.07; H 5.96; N 21.41.

2-(2H-Benzotriazol-2-yl)-3-dimethylamino-N,N-dimethyl-prop-2-eniminiumtetrafluoroborate (16): Phosphoryl chloride (9.30 ml, 101.90 mmol) was added dropwise to DMF (15.60 ml, 202.74 mmol) and the mixture stirred at 0 °C for 1 h. 2H-Benzotriazol-2-yl-acetic acid (6.00 g, 33.87 mmol) was added. After warming to 80 °C the mixture became first homogeneous, then a thick pale brown precipitate was formed. DMF (5 ml) was added and the mixture kept at 80 °C for 16 h. After cooling, methanol (40 ml) and afterwards a 50% aqueous solution of tetrafluoroboric acid (12.30 ml) were added and the brown precipitate collected by filtration. Yield 9.37 g (84%), pale-brown crystals that could be used for further reactions. 0.30 g of the crude product were dissolved in acetonitrile (20 ml) and after filtration diethyl ether (60 ml) was added to the filtrate. Yield 0.23 g (77%), colorless needles, m.p. 264-267 °C. IR (KBr): $\tilde{\nu}$ = 1625 cm^{-1}, 1408, 1303, 1204, 1123, 1083, 1062, 1038, 819, 759. UV/VIS (MeCN): λ_{max} (lg ε) = 210 nm (4.413), 301 (4.644). ^1H NMR ([D_6]DMSO): δ = 2.05 (s, 6 H, 2 NCH_3), 3.38 (s, 6H, 2 NCH_3), 7.56 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4'-H, 7'-H), 8.03 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5'-H, 6'-H), 8.09 (s, 2 H, 1-H, 3-H). Anal. Calcd. for $C_{13}H_{18}BF_4N_5$ (331.1): C 47.16; H 5.48; N 21.15. Found: C 47.28; H 5.51; N 21.23.

2-(1H-Benzotriazol-1-yl)-3-dimethylamino-N,N-dimethyl-prop-2-eniminium tetrafluoroborate (17): Phosphoryl chloride (9.30 ml, 101.90 mmol) was added dropwise to DMF (15.60 ml, 202.74 mmol) and the mixture stirred at 0 °C for 1 h. 2H-Benzotriazol-2-yl-acetic acid (6.00 g, 33.87 mmol) was added and the mixture warmed to 80 °C for 16 h. After cooling, methanol (40 ml) and afterwards a 50% aqueous solution of tetrafluoroboric acid (12.30 ml) were added and the precipitate collected by filtration. Yield 4.47 g (40%); pale-brown crystals. 0.30 g of the crude product were dissolved in acetonitrile (20 ml) and after fitration diethyl ether (60 ml) was added to the filtrate. Yield 0.19 g (63%), colorless needles, m.p. 186-188 °C. IR (KBr): $\tilde{\nu}$ = 1620 cm^{-1}, 1404, 1296, 1204, 1124, 1084, 1064, 103 7. UV/VIS (MeCN): λ_{max} (lg ε) = 252 nm (3.984), 304 (4.628). ^1H NMR ([D_6]DMSO): δ = 2.03 (s, 6 H, 2 NCH_3), 3.34 (s, 6 H, 2 NCH_3), 7.39-7.79 (m, 3 H, benzotriazolyl-H), 8.10 (m, 1 H, benzotriazolyl-H), 8.21 (s, 2 H, 1-H, 3-H). Anal. Calcd. for $C_{13}H_{18}BF_4N_5$ (331.1): C 47.16; H 5.48; N 21.15. Found: C 47.17; H 5.59; N 21.42.

2-(2-Methylthiopyrimidin-5-yl)-2H-benzotriazole (19a). General procedure: A mixture of **16** (0.50 g, 1.51 mmol) and methylthioformamidinium sulfate (0.21 g, 1.51 mmol) was refluxed in 10 ml of pyridine for 2 h. After cooling, the precipitate was collected by filtration and washed with water and hot methanol. Yield 0.26 g (71%), colorless crystals, m.p. 217 °C. IR (KBr): $\tilde{\nu}$ =1561 cm^{-1}, 1548, 1466, 1434, 1404, 1390, 1288, 1203, 962, 755. UV/VIS (toluene): λ_{max} = 332 nm; (DMSO): λ_{max} = 329 nm. ^1H NMR (CF_3CO_2D): δ = 3.00 (s, 3 H, SCH_3), 7.64 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4'-H, 7'-H), 8.00 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5'-H, 6'-H), 9.99 (s, 2 H, 4-H, 6-H). ^{13}C NMR (CF_3CO_2D): δ = 15.40 (SCH_3), 119.92 (C-4', C-7'), 132.42 (C-5', C-6'), 134.01 (C-5), 148.35 (C-3'a, C-7'a), 150.94 (C-4, C-6), 171.05 (C-2). Anal. Calcd. for $C_{11}H_9N_5S$ (243.3): C 54.31; H 3.73; N 28.79; S 13.18. Found: C 54.63; H 3.84; N 28.78; S 13.18.

2-(2-Dimethylaminopyrimidin-5-yl)-2H-benzotriazole (19b): From **16** (0.50 g, 1.51 mmol) and 1,1-dimethylguanidinium sulfate (0.21 g, 1.54 mmol). Yield 0.14 g (39%), pale-brown crystals, m.p. 246-247 °C. IR (KBr): $\tilde{\nu}$ = 1606 cm^{-1}, 1567, 1549, 1407, 1393, 792, 751, 747. UV/VIS (toluene): λ_{max} (lg ε) = 337 nm (4.332); (DMSO): λ_{max} (lg ε) = 337 nm (4.304). ^{1}H NMR (CF_3CO_2D): δ = 3.60 (s, 6 H, $N(CH_3)_2$), 7.67 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4'-H, 7'-H), 8.01 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5'-H, 6'-H), 9.59 (s, 2 H, 4-H, 6-H). ^{13}C NMR (CF_3CO_2D): δ = 39.78 ($N(CH_3)_2$), 119.47 (C-4', C-7'), 127.45 (C-5), 132.15 (C-5', C-6'), 147.49 (C-3'a, C-7'a), 150.91 (C-4, C-6), 154.42 (C-2). Anal. Calcd. for $C_{12}H_{12}N_6$ (240.3): C 59.99; H 5.03; N 34.98. Found: C 59.70; H 5.05; N 34.99.

2-(2-Methylpyrimidin-5-yl)-2H-benzotriazole (19c): From **16** (1.00 g, 3.02 mmol) and acetamidinium chloride (0.29 g, 3.07 mmol). Yield 0.19 g (30%), pale-brown microcrystalline powder, m.p. 180-182 °C. After evaporation of the solvents, further 0.37 g (58%) of **19c** were obtained. IR (KBr): $\tilde{\nu}$ = 1563 cm^{-1}, 1473, 1442, 1415, 1290, 967, 752, 740. UV/VIS ($CHCl_3$): λ_{max} (lg ε) = 312 nm (4.379). ^{1}H NMR ($CHCl_3$): δ = 2.85 (s, 3 H, 2'-CH_3), 7.44 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4-H, 7-H), 7.91 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5-H, 6-H), 9.55 (s, 2 H, 4'-H, 6'-H). ^{13}C NMR ($CHCl_3$): δ = 25.78 (2'-CH_3), 118.38 (C-4, C-7), 128.00 (C-5, C-6), 132.82 (C-5'), 145.32 (C-3a, C-7a), 148.63 (C-4', C-6'), 168.19 (C-2'). Anal. Calcd. for $C_{11}H_9N_5$ (211.2): C 62.55; H 4.29; N 33.16. Found: C 62.19; H 4.23; N 33.03.

2-(2-Dimethylaminovinylpyrimidin-5-yl]-2H-benzotriazole (19d): The solution of **19c** (0.22 g, 1.04 mmol) and *tert*-butyloxy-bis-dimethylamino-methane **9** (0.90 ml, 4.36 mmol) in 10 ml of DMF was stirred at 120 °C for 16 h. The precipitate was collected by filtration and washed with hot methanol. Yield 0.23 g (83%), yellow microcrystalline powder, m.p. 226-228 °C. IR (KBr): $\tilde{\nu}$ = 1631 cm^{-1}, 1576, 1569, 1559, 1467, 1439, 1380, 1358, 1274, 1099. UV/VIS (toluene): λ_{max} (lg ε) = 396 nm (4.649); (DMSO): λ_{max} (lg ε) = 290 nm (4.043), 404 (4.627). ^{1}H NMR ($CDCl_3$): δ = 3.00 (s, 6 H, $N(CH_3)_2$), 5.40 (d, J = 13 Hz, 1 H, 1"-H), 7.42 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4-H, 7-H), 7.90 (d, J = 13 Hz, 1 H, 2"-H), 7.91 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5-H, 6-H), 9.29 (s, 2 H, 4'-H, 6'-H). ^{13}C NMR ($CDCl_3$): δ = 41.00 (br, $N(CH_3)_2$), 94.90 (C-1"), 118.04 (C-4, C-7), 127.24 (C-5, C-6), 129.17 (C-5'), 144.98 (C-3a, C-7a), 148.82 (C-4', C-6'), 149.80 (C-2"), 167.55 (C-2'). Anal. Calcd. for $C_{14}H_{14}N_6$ (266.3): C 63.14; H 5.30; N 31.56. Found: C 63.11; H 5.59; N 31.39.

2-[2-(4-Nitrophenyl)-pyrimidin-5-yl]-2H-benzotriazole (19e): From **16** (0.49 g, 1.48 mmol) and *p*-nitrobenzamidine hydrochloride (0.21 g, 1.54 mmol). Yield 0.41 g (87%), pale-brown powder, m.p. > 340 °C. IR (KBr): $\tilde{\nu}$ = 1557 cm^{-1}, 1516, 1470, 1436, 1410, 1339, 1288, 959, 761, 744. UV/VIS (DMSO): λ_{max} = 342 nm. ^{1}H NMR (CF_3CO_2D): δ = 7.66-7.70 (m, 2 H, 4-H, 7-H), 8.02-8.06 (m, 2 H, 5-H, 6-H), 8.64 (d, J = 9Hz, 2 H, 3"-H, 5"-H), 8.68 (d, J = 9 Hz, 2 H, 2"-H, 6"-H), 10.34 (s, 2 H, 4'-H, 6'-H). Anal. Calcd. for $C_{16}H_{10}N_6O_2$ (318.3): C 60.38; H 3.17; N 26.40. Found: C 60.42; H 3.26; N 26.36.

2-[2-(4-Aminophenyl)-pyrimidin-5-yl]-2H-benzotriazole (19f): From **16** (0.50 g, 1.51 mmol) and of *p*-aminobenzamidine dihydrochloride (0.31 g, 1.49 mmol). Yield 0.28 g (65%), fine orange powder, m.p. > 340 °C. IR (KBr): $\tilde{\nu}$ = 1651 cm^{-1}, 1604, 1554, 1544, 1467, 1431, 1406, 1283. UV/VIS (DMSO): λ_{max} = 321 nm, 434. ^{1}H NMR (CF_3CO_2D): δ = 7.71 (d, J = 8 Hz, 2 H, 3"-H, 5"-H), 8.02-8.09 (m, 4 H, benzotriazolyl-H), 8.82 (d, J = 8 Hz, 2 H, 2"-H, 6"-H), 10.37 (s, 2 H, 4'-H, 6'-H). Anal. Calcd. for $C_{16}H_{12}N_6$ (288.3): C 66.66; H 4.20; N 29.15. Found: C 67.31; H 3.73; N 28.91.

1-(2-Methylthiopyrimidin-5-yl)-1H-benzotriazole (20a): From **17** (0.50 g, 1.51 mmol) and methylthioformamidium sulfate (0.21 g, 1.51 mmol) (20 h refluxing). The solvent was evaporated, water added to the residue and the remaining solid washed with water and recrystallized from aqueous ethanol. Yield 0.22 g (60%), colorless powder, m.p. 161-162 °C. IR (KBr): $\tilde{\nu}$ = 1536 cm^{-}

[1], 1489, 1463, 1437, 1393, 1213, 1067, 766, 739. UV/VIS (toluene): λ_{max} (lg ε) = 303 nm (4.162); (DMSO): λ_{max} (lg ε) = 270 nm (4.388), 300 (4.158). ^{1}H NMR ($CDCl_3$): δ = 2.67 (s, 3 H, SCH_3), 7.50 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, 5'-H), 7.63 (ddd, ^3J = 8 Hz, ^3J = 8 Hz, ^4J = 1 Hz, 1 H, 6'-H), 7.69 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^4J = 1 Hz, 1 H, 7'-H), 8.18 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^4J = 1 Hz, 1 H, 4'-H), 9.00 (s, 2 H, 4-H, 6-H). ^{13}C NMR ($CDCl_3$): δ = 14.58 (SCH_3), 109.37 (C-7'), 120.82 (C-4'), 124.97 (C-5'), 128.31 (C-5), 129.16 (C-6'), 132.19 (C-7'a), 146.51 (C-3'a), 150.87 (C-4, C-6), 173.14 (C-2). Anal. Calcd. for $C_{11}H_9N_5S$ (243.3): C 54.31; H 3.73; N 28.79; S 13.18. Found: C 54.46; H 3.72; N 28.78; S 13.16.

1-(2-Dimethylaminopyrimidin-5-yl)-1H-benzotriazole (20b): From **17** (0.50 g, 1.51 mmol) and *N,N*-dimethylguanidinium sulfate (0.21 g, 1.54 mmol). Yield 0.12 g (33%), colorless powder, m.p. 140-142 °C. IR (KBr): $\tilde{\nu}$ = 1610 cm^{-1}, 1541, 1488, 1461, 1411, 1280, 1072, 791, 785, 741. UV/VIS (toluene): λ_{max} (lg ε) = 301 nm (4.029); (DMSO): λ_{max} (lg ε) = 262 nm (4.382), 300 (4.011). ^{1}H NMR ($CDCl_3$): δ = 3.30 (s, 6 H, $N(CH_3)_2$), 7.44 (ddd, ^3J = 8 Hz, ^3J = 6 Hz, ^4J = 2 Hz, 1 H, 5'-H), 7.52-7.58 (m, 2 H, 6'-H, 7'-H), 8.14 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^4J = 1 Hz, 1 H, 4'-H), 8.63 (s, 2 H, 4-H, 6-H). ^{13}C NMR ($CDCl_3$): δ = 37.47 ($N(CH_3)_2$), 109.53 (C-7'), 120.37 (C-4'), 121.40 (C-5), 124.41 (C-5'), 128.36 (C-6'), 133.20 (C-7'a), 146.17 (C-3'a), 153.05 (C-4, C-6), 161 .71 (C-2). Anal. Calcd. for $C_{12}H_{12}N_6$ (240.3): C 59.99; H 5.03; N 34.98. Found: C 60.08: H 5.12; N 34.84.

1-(2-Methylpyrimidin-5-yl)-1H-benzotriazole (20c): From **17** (1.00 g, 3 .02 mmol) and acetamidinium chloride (0.29 g, 3.07 mmol) (20 h refluxing). The solvent was evaporated, the residue treated with water and the remaining solid washed with water and a little methanol. Yield 0.20 g (31%), light brown needles, m.p. 165-167 °C. IR (KBr): $\tilde{\nu}$ = 3034 cm^{-1}, 1554, 1492, 1472, 1454, 1268, 1044, 783, 744, 735. UV/VIS ($CHCl_3$): λ_{max} = 297 nm. ^{1}H NMR ($CDCl_3$): δ = 2.90 (s, 3 H, 2'-CH_3), 7.51 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, 5-H), 7.65 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, 6-H), 7.73 (dm, ^3J = 8 Hz, 1 H, 7-H), 8.20 (dm, ^3J = 8 Hz, 1 H, 4-H), 9.15 (s, 2 H, 4'-H, 6'-H). ^{13}C NMR ($CDCl_3$): δ = 25.85 (2'-CH_3), 109.41 (C-7), 120.89 (C-4), 125.04 (C-5), 129.25 (C-6), 130.13 (C-5'), 132.12 (C-7a), 146.61 (C-3a), 150.43 (C-4', C-6'), 168.35 (C-2'). Anal. Calcd. for $C_{11}H_9N_5$ (211.2): C 62.55; H 4.29; N 33.16. Found: C 62.38; H 4.26; N 33.15.

1-(2-Dimethylaminovinylpyrimidin-5-yl)-1H-benzotriazole (20d): The solution of **20c** (0.10 g, 0.47 mmol) and *tert*-butyloxy-bis-dimethylaminomethane **9** (0.20 ml, 0.97 mmol) in DMF (5 ml) was stirred at 120 °C for 12 h. The solvent was evaporated and the residue washed several times with methanol. Yield 0.11 g (88%), light yellow powder, m.p. 188-191 °C. IR (KBr): $\tilde{\nu}$ = 1636 cm^{-1}, 1587, 1490, 1465, 1375, 1278, 1104. UV/VIS (toluene): λ_{max} (lg ε) = 352 nm (4.470); (DMSO): λ_{max} (lg ε) = 357 nm (4.484). ^{1}H NMR ($CDCl_3$): δ = 3.03 (s, 6 H, $N(CH_3)_2$), 5.40 (d, J = 13 Hz, 1 H, 1"-H), 7.46 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, 5-H), 7.58 (ddd, ^3J = 8 Hz, ^3J = 7 Hz, ^4J = 1 Hz, 1 H, 6-H), 7.64 (ddd, ^3J = 8 Hz, ^3J = 1 Hz, ^4J = 1 Hz, 1 H, 7-H), 7.91 (d, J = 13 Hz, 1 H, 2"-H), 8.16 (ddd, ^3J = 8 Hz, ^4J = 1 Hz, ^4J = 1 Hz, 1 H, 4-H), 8.76 (s, 2 H, 4'-H, 6'-H). ^{13}C NMR ($CDCl_3$): δ = 94.53 (C-1"), 109.64 (C-7), 120.51 (C-4), 124.57 (C-5), 125.48 (C-5'), 128.58 (C-6), 132.61 (C-7a), 146.33 (C-3a), 149.97 (C-2"), 151.17 (C-4', C-6'), 167.88 (C-2'). Anal. Calcd. for $C_{14}H_{14}N_6$ (266.3): C 63.14; H 5.30; N 31.56. Found: C 63.38; H 5.15; N 31.46.

1-[2-(4-Nitrophenyl)-pyrimidin-5-yl]-1H-benzotriazole (20e): From **17** (0.49 g, 1.48 mmol) and *p*-nitrobenzamidinium hydrochloride (0.30 g, 1.49 mmol). The precipitate was washed with hot water, boiling acetonitrile and methanol. Yield 0.39 g (83%) pale-brown powder, m.p. > 340 °C. IR (KBr): $\tilde{\nu}$ =1582 cm^{-1}, 1549, 1514, 1485, 1462, 1455, 1343, 1044, 867, 755, 742. UV/VIS (DMSO): λ_{max} (lg ε) = 321 nm (4.297). ^{1}H NMR (CF_3CO_2D): δ = 7.95-8.39 (m, 4 H, benzotriazolyl-H), 8.58 (d, J = 9Hz, 2 H, 3"-H, 5"-H), 8.66 (d, J = 9 Hz, 2H, 2"-H, 6"-H), 9.80 (s, 2 H, 4'-H, 6'-H). Anal. Calcd. for $C_{14}H_{14}N_6$ (318.3): C 60.38; H 3.17; N 26.40. Found: C 60.51; H 3.46; N 26.33.

4-[N-(*p*-Ethoxybenzylidene)-*N*-methylhydrazino]-benzaldehyde (24a). General procedure: A 1.6 M solution of *tert*-butyllithium in pentane (14.70 ml, 23.52 mmol) was added dropwise under stirring to a pale yellow suspension of 4-ethoxybenzaldehyde-*N*-(*p*-bromophenyl)-*N*-methylhydrazone (3.88 g, 11.64 mmol) in THF (50 ml) at –78 °C, and the mixture was stirred for 1 h. *N*-methylformanilide (1.50 ml, 12.21 mmol) in THF (10 ml) was added dropwise under stirring. After 8 h at room temperature, 1 N HCl (50 ml) was added and the mixture extracted 3 times with chloroform (30 ml), the combined organic phases dried with sodium sulfate and after filtration evaporated to almost dryness. After having added methanol (10 ml) to the warm residue the solution was cooled to 0 °C, the precipitate isolated by filtration and recrystallized from methanol (50 ml). Yield 2.23 g (71%), yellow-green needles, m.p. 128 °C. IR (KBr): $\tilde{\nu}$ = 1675 cm^{-1}, 1600, 1560, 1512, 1392, 1249, 1172, 1104. UV/VIS (toluene): λ_{max} (lg ε) = 306 nm (3.958), 368 (4.596), 381 (4.603), ($CHCl_3$): λ_{max} (lg ε) = 240 nm (4.112), 255 (4.106), 267 (sh, 4.055), 299 (3.981), 381 (4.651), 682 (2.907); (CH_3CN): λ_{max} (lg ε) = 244 nm (4.135), 267 (4.046), 306 (4.029), 377 (4.635), (DMSO): λ_{max} (lg ε) = 272 nm (4.026), 305 (3.938), 385 (4.631). ^{1}H NMR ($CDCl_3$): δ = 1.41 (t, J = 7 Hz, 3 H, $CH_2C\underline{H}_3$), 3.37 (s, 3 H, NCH_3), 4.04 (q, J = 7 Hz, 2 H, $C\underline{H}_2CH_3$), 6.90 (d, J = 9 Hz, 2H, 3"-H, 5"-H), 7.45 (d, J = 9 Hz, 2 H, 3-H, 5-H), 7.56 (s, 1 H, CH=N), 7.62 (d, J = 9 Hz, 2 H, 2"-H, 6"-H), 7.78 (d, J = 9 Hz, 2 H, 2-H, 6-H), 9.80 (s, 1H, CH=O). ^{13}C NMR ($CDCl_3$): δ = 14.78 ($CH_2\underline{C}H_3$), 32 13 (NCH_3), 63.52 ($\underline{C}H_2CH_3$), 113.68 (C-3, C-5), 114.70 (C-3", C'-5"), 127.32 (C-1), 127.99 (C-2", C-6"), 128.38 (C-1"), 131.50 (C-2, C-6), 135.50 (CH=N), 152.14 (C-4), 159.65 (C-4"), 190.60 (CH=O). - MS (70 eV), *m/z* (%): 282 (17) [M^+], 281 (100). Anal. Calcd. for $C_{17}H_{18}N_2O_2$ (282.3): C 72.32; H 6.43; N 9.92. Found: C 71.90; H 6.33; N 10.04.

4-[*N*-Methyl-*N'*-(4-methylthiobenzylidene)-hydrazino]-benzaldehyde (24b): From 4-methylthiobenzaldehyde-*N*-(4-bromophenyl)-*N*-methylhydrazone (3.79 g, 11.30 mmol). Yield 2.40 g (75%); orange needles, m.p. 125-128 °C. IR (KBr): $\tilde{\nu}$ = 1672 cm^{-1}, 1603, 1594, 1565, 1514, 1390, 1332, 1168, 1119, 1105, 1090. UV/VIS (toluene): λ_{max} (lg ε) = 291 nm (4.215), 373 (4.640), 387 (4.636), ($CHCl_3$): λ_{max} (lg ε) = 291 nm (4.180), 377 (4.694), 387 (4.702), 691 (2.597), (CH_3CN): λ_{max} (lg ε) = 226 nm (4.136), 243 (4.121), 287 (4.184), 374 (4.698), 382 (4.703), (DMSO): λ_{max} (lg ε) = 292 nm (4.157), 383 (4.664), 391 (4.670). ^{1}H NMR ($CDCl_3$): δ = 2.49 (s, 3 H, SCH_3), 3.41 (s, 3 H, NCH_3), 7.24 (d, J = 8 Hz, 2 H, 3"-H, 5"-H), 7.43 (d, J = 9 Hz, 2 H, 3-H, 5-H), 7.56 (s, 1 H, CH=N), 7.61 (d, J = 8 Hz, 2H, 2"-H, 6"-H), 7.80 (d, J = 9 Hz, 2 H, 2-H, 6-H), 9.83 (s, 1H, CH=O). ^{13}C NMR ($CDCl_3$): δ = 15.55 (SCH_3), 32.26 (NCH_3), 113.95 (C-3, C-5), 126.38 (C-3", C-5"), 126.41 (C-1), 126.93 (C-2", C-6"), 128.99 (C-1"), 131.48 (C-2, C-6), 134.88 (CH=N), 139.46 (C-4"), 151.99 (C-4), 190.61 (CH=O). MS (70 eV), *m/z* (%): 286 (6) [M^+ + 2], 285 (19) [M^+ + 1], 284 (100) [M^+]. Anal. Calcd. for $C_{16}H_{16}N_2OS$ (284.4): C 67.58; H 5.67; N 9.85; S 11.27. Found: C 67.33; H 5.77; N 9.91; S 11.28.

4-[*N'*-(4-Dimethylaminobenzylidene-*N*-methyl-hydrazino]-benzaldehyde (24c): From 4-dimethylaminobenzaldehyde-*N*-(4-bromophenyl)-*N*-methylhydrazone (4.00 g, 12.04 mmol) [work-up with water (10 ml); after having added chloroform (50 ml) the organic phase was extracted 5 times with water (30 ml), dried over Na_2SO_4, filtered and the filtrate was evaporated almost to dryness; methanol (10 ml) was added to the still warm yellow residue, the precipitate isolated by filtration and recrystallized from methanol (100 ml); evaporation of the mother liquor and addition of methanol (10 ml) yielded a second fraction]. Yield 2.50 g (74%), yellow-orange crystals, m.p. 174-175 °C. IR (KBr): $\tilde{\nu}$ = 1663 cm^{-1}, 1594, 1560, 1515, 1394, 1166, 1107. UV/VIS (toluene): λ_{max} (lg ε) = 302 nm (4.240), 387 (4.570); ($CHCl_3$): λ_{max} (lg ε) = 303 nm (4.255), 397 (4.633); (MeCN): λ_{max} (lg ε) =225 nm (4.184), 298 (4.294), 393 (4.700); (DMSO): λ_{max} (lg ε) = 303 nm (4.248), 402 (4.629). ^{1}H NMR ($CDCl_3$): δ = 2.98 (s, 6 H, $N(CH_3)_2$), 3.36 (s, 3 H, NCH_3), 6.70 (d, J = 9Hz, 2 H, 3"-H, 5"-H), 7.40 (d, J = 9 Hz, 2 H, 3-H, 5-H), 7.57 (s, 1 H, CH=N), 7.58 (d, J = 9 Hz, 2 H, 2"-H, 6"-H), 7.77 (d, J = 9 Hz, 2 H, 2-H, 6-H), 9.79 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$): δ = 32.08 (NCH_3), 40.26 ($N(CH_3)_2$), 112.08 (C-3", C-5"), 113.39 (C-3, C-5), 123.82 (C-1"), 127.90 (C-2", C-6"), 127.96 (C-1), 131.52 (C-2, C-6), 136.78 (CH=N), 150.92 (C-4 or C-4"), 152.28 (C-4" or C-

4), 190.53 (CHO). MS (70 eV), *m/z* (%): 282 (18) [$M^+ + 1$], 281 (100) [M^+], 147 (26), 140.5 (6) [M^{2+}]. Anal. Calcd. for $C_{17}H_{19}N_3O$ (281.4): C 72.57; H 6.81; N 14.94. Found: C 72.37; H 6.71; N 14.89.

4-Dimethylaminobenzaldehyde-*N*-{4-[2-(2H-benzotriazol-2-yl)-vinyl]-phenyl}-*N*-methyl-hydrazone (25): A 1.6 M solution of butyllithium in hexane (0.90 ml, 1.44 mmol) was added dropwise under stirring to a solution of 2-trimethylsilylmethyl-2H-benzotriazole **23**[6,26] (0.29 g, 1.42 mmol) in THF (7 ml) at –78 °C. After stirring the blue solution for 1 h at –78 °C, a solution of **24c** (0.40 g, 1.42 mmol) in THF (10 ml) was added. The mixture was warmed slowly to room temperature and after 8 h poured into a saturated aqueous solution of NH_4Cl (20 ml). The aqueous phase was extracted 3 times with 20-ml portions of chloroform. The combined organic phases were washed with water (20 ml), dried over Na_2SO_4, and the solvent was removed in vacuo. Pentane was added to the dark brown residue, the resulting precipitate isolated by filtration and recrystallized from methanol. Yield 0.29 g (52%), green-brown powder, m.p. 229-231 °C. IR (KBr): $\tilde{\nu}$ = 1603 cm^{-1}, 1514, 1388, 1188, 1107. UV/VIS (toluene): λ_{max} (lg ε) = 323 nm (4.368), 367 (sh, 4.348), 417 (4.525); (DMSO): λ_{max} (lg ε) = 326 nm (4.372), 371 (4.345), 427 (4.511). ^1H NMR ($CDCl_3$): δ = 3.00 (s, 6 H, $N(CH_3)_2$), 3.42 (s, 3 H, NCH_3), 6.74 (d, J = 9 Hz, 2 H, 3-H, 5-H), 7.39 (dd, ^3J = 6 Hz, ^4J = 3 Hz, 2 H, 4'''-H, 7'''-H), 7.40 (d, J = 9 Hz, 2 H, 2'-H, 6'-H), 7.51 (d, J = 9 Hz, 2 H, 3'-H, 5'-H), 7.55 (s, 1 H, CH=N), 7.61 (d, J = 9 Hz, 2 H, 2-H, 6-H), 7.80 (d, J = 14 Hz, 1 H, 2''-H), 7.87 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5'''-H, 6'''-H), 7.94 (d, J = 14 Hz, 1 H, 1''-H), 9.29 (s, 2 H, 4'-H, 6'-H). MS (70 eV), *m/z* (%): 397 (26) [$M^+ + 1$], 396 (100) [M^+], 250 (22), 145 (26), 131 (23), 130 (23). Anal. Calcd. for $C_{24}H_{24}N_6$ (396.5): C 72.70; H 6.10; N 21.20. Found: C 72.25; H 6.22; N 21.29.

4-[*N'*-(4-Ethoxybenzylidene)-*N*-methylhydrazino]-benzonitrile : 4-[*N*-(4-Ethoxybenzylidene)-hydrazino]-benzonitrile (1.20 g, 4.52 mmol) was added under stirring at room temperature to NaH (0.20 g, 5.00 mmol; 60% suspension in mineral oil) in THF. Dimethyl sulfate (0.50 ml, 5.27 mmol) in THF (5 ml) was added to the mixture, which was stirred at room temperature for 12 h and then refluxed for 1 h. After cooling, aqueous NH_3 (50 ml) was added dropwise, the aqueous phase extracted 3 times with Et_2O, the combined organic phases were dried over Na_2SO_4, evaporated to dryness and the residue was recrystallized from 100 ml of ethanol. Yield 0.94 g (75%), pale-brown needles, m.p. 140-141 °C. Anal. Calcd. for $C_{17}H_{17}N_3O$ (279.3): C 73.10; H 6.13; N 15.05. Found: C 73.19; H 6.24; N 14.94.

4-[*N''*-(4-Ethoxybenzylidene)-*N'*-methylhydrazino]-*N,N*-tris(trimethylsilyl)-benzamidine (26): A solution of 4-[*N'*-(4-ethoxybenzylidene)-*N*-methylhydrazino]-benzonitrile (1.20 g, 4.30 mmol) and *N*-lithiumhexamethyldisilazane (1.44 g, 8.61 mmol) in Et_2O (50 ml) was stirred at room temperature for 24 h. The solvent was evaporated and the remaining brown oil dissolved in toluene (50 ml). Chlorotrimethylsilane (1.10 ml, 8.71 mmol)) was added and the solution refluxed for 10 h. The precipitate was removed by filtration and the filtrate evaporated to dryness. The residue was extracted 3 times with 30-ml protions of pentane. After evaporation of the solvent, 1.50 g (68%) of a brown oil were obtained which was used directly for the preparation of **27**.

4-Ethoxybenzaldehyde-*N*-{4-[5-(2H-benzotriazol-2-yl)-pyrimidin-2-yl]-phenyl}-*N*-methyl-hydrazone (27): The mixture of 4-[*N''*-(4-ethoxybenzylidene)-*N'*-methylhydrazino]-*N,N*-tris-(trimethylsilyl)-benzamidine **26** (0.60 g, 1.17 mmol), **17** (0.39 g, 1.18 mmol) and KF (0.21 g, 3.62 mmol) in pyridine (20 ml) was refluxed for 3 h. The precipitate was isolated by filtration, washed with water and hot ethanol and recrystallized from toluene. Yield 0.36 g (69%), yellow microcrystalline powder, m.p. 319-320 °C. IR (KBr): $\tilde{\nu}$ = 1606 cm^{-1}, 1577, 1564, 1510, 1466, 1434, 1406, 1388, 1246, 1108. UV/VIS (toluene): λ_{max} = 310 nm, 416; (DMSO): ; λ_{max} = 276 nm, 310, 419. ^1H NMR (CF_3CO_2H): δ =1.58 (t, J = 7 Hz, 3 H, $OCH_2\underline{CH_3}$), 3.71 (s, 3 H, NCH_3), 4.37 (q, J = 7 Hz, 2 H, $OC\underline{H_2}CH3$), 7.26 (d, J = 9 Hz, 2 H, 3-H, 5-H), 7.31 (d, J = 9 Hz, 2 H, 2'-H, 6'-H), 7.62 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 4'''-H, 7'''-H), 8.00 (dd, ^3J = 7 Hz, ^4J = 3 Hz, 2 H, 5'''-H, 6'''-H), 8.18 (d, J = 9 Hz, 2 H, 2-H, 6-H), 8.54 (d, J = 9 Hz, 2 H, 3'-H, 5'-H), 8.89 (s, 1 H, CH=N), 10.17 (s, 2 H, 4''-H, 6''-H). Anal. Calcd. for $C_{26}H_{23}N_7O$ (449.5): C 69.47; H 5.16; N 21.81. Found: C 69.21; H 5.26; N 21.86.

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References

1. a) D. J. Williams, *Angew. Chem.* **1984**, *96*, 637-651; *Angew. Chem. Int. Ed. Eng.* **1984**, *23*, 690-704. b) D. J. Williams (Ed.), *Nonlinear Optical Properties of Organic and Polymeric Materials, ACS Symp. Ser. 233,* **1983**. c) D. S. Chemla, J. Zyss (Eds),*Nonlinear Optical Properties of Organic Molecules and Crystals,* Academic Press, Orlando **1987**. d) P. N. Prasad, D. J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers,* John Wiley, New York, **1991**. e) S. Marder, J. Sohn, G. Stucky (Eds.), *Materials for Nonlinear Optics: Chemical Perspectives, ACS Symp. Ser. 455,* **1991**. f) R. A. Hann, D. Bloor (Eds.), *Organic Materials for Non-limear Optics,* Royal Society of Chemistry, Special Publication 69, **1989**. g) R. A. Hann, D. Bloor (Eds.), *Organic Materials for Non-linear Optics II,* Royal Society of Chemistry, Special Publication 91, **1991**. h) S. R. Marder, J. W. Perry, *Adv. Mater.* **1993**, *5*, 804-815. i) W. Nie, *ibid* **1993**, *5*, 520-545. h) D. F. Eaton, *Science* **1991**, *253,* 281-287.
2. *Magnetic Molecular Materials* (D. Gatteschi, O. Kahn, J. S. Miller, F. Palacio, Eds.), *NATO ASI Series E*, Vol. *198,* Kluwer Academic Publishers, Dordrecht, **1991**.
3. a) D. O. Cowan, F. M. Wiygul, *Chem. & Eng News* 21. Juli **1986**, 28. b) M. R. Bryce, *Chem. Soc. Rev.* **1991**, *20,* 355-390.
4. J. S. Miller, *Adv. Mater.* **1990**, *2*, 378-379, 495-497, 601-603.
5. a) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95,* 10631-10643. b) L. T. Cheng, W. Tam, S. R. Marder, A. W. Stiegman, G. Rikken, C. W. Spangler, *ibid.* **1991**, *95,* 10643-10652.
6. a) A. R. Katritzky, J. N. Lam, *Heteroatom Chemistry* **1990**, *1*, 21-31, and references cited therein. b) A. R. Katritzky, Z. Yang, J. N. Lam, *Synthesis* **1990**, 666-669. c) A. R. Katritzky, S. Rachwal, G. J. Hitchings, *Tetrahedron* **1991**, *47*, 2683-2732.
7. W. König, R. Geiger, *Chem. Ber.* **1970**, *103*, 788-798.
8. H. Wamhoff in *Comprehensive Heterocyclic Chemistry* (A. R. Katritzky, C. W. Rees, Eds.), Pergamon Press, Oxford , **1984,** Vol. *5*, part 4A, chapter 4.11.
9. M. Dexter in *Encyclopedia of Chemical Technology,* 3. ed., Wiley-Interscience, New York, **1983**, Vol. *23*, p. 615.
10. M. Okazaki, S. Kubodera, H. Fukunaga (Fuji Photo Film Co., Ltd.), Jpn. Kokai Tokkyo Koho JP 01,187, 538, **1989**; *Chem. Abstr.* **1990**, *112*, P 168791p.
11. C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.* **1991**, *91*, 165-195.
12. K. Elbs, *J. Prakt. Chem.* **1924**, *108*, 209-233.
13. R. Nietzki, O. Baur, *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 2977-2986.
14. J. L. Riebsomer, *J. Org. Chem.* **1948**, *13*, 815-821.
15. a) B. B. Corson, R. W. Stoughton, *J. Am. Chem. Soc.* **1928**, *50*, 2825-2837. b) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, H. F. Mower, *J. Am. Chem. Soc.* **1958**, *80*, 2806-2815.

16. F. Krollpfeiffer, A. Rosenberg, C. Mühlhausen, *Liebigs Ann. Chem.* **1935**, *515*, 113-130.
17. a) E. G. McRae, *J. Phys. Chem.* **1957**, *61*, 562-572. b) M. S. Paley, J. M. Harris, H. Looser, J. C. Baumert, G. C. Bjorklund, D. Jundt, R. J. Twieg, *J. Org. Chem.* **1989**, *54*, 37743778. c) G. Bacquet, P. Bassoul, C. Combellas, J. Simon, A. Thiébault, F. Tournilhac, *Adv. Mater.* **1990**, *2*, 311-313. d) D. M. Burland, R. D. Miller, O. Reiser, R. J. Twieg, C. A. Walsh, *J. Appl. Phys.* **1992**, *71*, 410-417. e) Ch. Bosshard, G. Knöpfle, P. Prêtre, P. Günter, *ibid.* **1992**, *71*, 1594-1605. f) R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J.-L. Brédas, B. M. Pierce, *Science* **1994**, *265*, 632-635.
18. F. Sparatore, F. Pagani, *Ann. Chim.* **1962**, *52*, 248-258.
19. R. J. Twieg, K. Jain, *ACS Symp. Ser. 233*, **1983**, p. 57.
20. a) R. M. Wagner, C. Jutz, *Chem. Ber.* **1971**, *104*, 2975-2983. b) Z. Arnold, *Collect. Czech. Chem. Commun.* **1965**, *30*, 2125-2127. c) F. Adams, R. Gompper, E. Kujath, *Angew. Chem.* **1989**, *101*, 1043-1048; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1060-1065. d) H. Zaschke, S. Arndt, V. Wagner, H. Schubert, *Z. Chem.* **1977**, *17*, 293-294.
21. P. Walther, Ph. D. thesis, Universität München **1993**.
22. J. T. Gupton, F. A. Hicks, S. Q. Smith, A. D. Main, S. A. Petrich, D. R. Wilkinson, J. A. Sikorski, A. R. Katritzky, *Tetrahedron* **1993**, *49*, 10205-10218.
23. J. Zyss, I. Ledoux, M. Bertault, E. Toupet, *Chem. Phys.* **1991**, *150*, 125-135.
24. a) W. Tam, L.-T. Cheng, J. D. Bierlein, L. K. Cheng, Y. Wang, A. E. Feiring, G. R. Meredith, D. F. Eaton, J. C. Calabrese, G. L. J. A. Rikken, *ACS Symp. Ser. 455*, **1991**, 158-169. b) G. Berkovic, Y. R. Shen, M. Schadt, *Mol. Cryst. Liq. Cryst. B* **1987**, *150*, 607-616.
25. a) D. Lupo, W. Prass, U. Scheunemann, A. Laschewsky, H. Ringsdorf, I. Ledoux, *J. Opt. Chem. Soc. Am. B* **1988**, *5*, 300-308. b) C. Bubeck, A. Laschewsky, D. Lupo, D. Neher, P. Ottenbreit, W. Paulus, W. Prass, H. Ringsdorf, G. Wegner, *Adv. Mater.* **1991**, *3*, 54-58.
26. a) D. J. Peterson, *J. Org. Chem.* **1968**, *33*, 780. b) D. A. Jager, *Synthesis* **1984**, 384-389.
27. A. R. Katritzky, R. J. Offerman, P. Cabildo, M. Soleiman, *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 641-645.
28. a) A. R. Sanger, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 351-354. b) A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, *J. Am. Chem. Soc.* **1992**, *114*, 5000-5004. c) R. T. Boere, R. T. Oakley, R. W. Reed, *J. Organomet. Chem.* **1987**, *331*, 161-167. d) K. Dehnicke, *Chem.-Ztg.* **1990**, *114*, 295-304. e) R. Akabe, K. Tokumaru, T. Kobayashi, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1993-2001.
29. S. Brandl, R. Gompper, K. Polborn, *J. Prakt. Chem.* **1996**, *338*, 451-459; S. Brandl, Ph. D. thesis, Universität München **1994**.
30. Canon K. K. Copyer Co., Ltd., Jpn Kokai Tokkyo Koho Jp 5809,150, **1983**; Chem. Abstr. **1984**, *101*, P 31084p.
31. B. A. Reinhardt, R. Kannan, A. G. Dillhardt, SPIE **1993**, *50*, 1853.
32. K. Clays, A. Persoons, *Phys. Rev. Lett.* **1991**, *66*, 2980-2983.
33. M. Stähelin, D. M. Burland, J. E. Rice, *Chem. Phys. Lett.* **1992**, *191*, 245-250.
34. K. Clays, A. Persoons, *Rev. Sci. Instrum.* **1992**, *63*, 3285-3289.

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