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Push–Pull Azo-Chromophores Containing Two Fused Pentatomic Heterocycles and Their Nonlinear Optical Properties

Roberto Centore,*[a] Sandra Fusco,[a] Andrea Peluso,[b] Amedeo Capobianco,[b] Matthias Stolte,[c] Graziano Archetti,[c] and Hans-Georg Kuball*[c]

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We have developed procedures for the synthesis of push–pull azo-chromophores containing the *s*-triazolo[3,4-*b*]thiadiazole heterocycle compatible with the presence of electron-acceptor groups (nitrophenyl group) as substituents on both the triazole and thiadiazole rings. The linear and non-linear optical properties of the synthesized chromophores have been characterized by the EFISH technique, electro-optical absorption spectroscopy and DFT calculations. The combined results indicate a significant modulation of the properties of the chromophores depending on the substitution pattern on the heterobicycle. Fast UV-driven *trans* → *cis* and slower thermally driven *cis* → *trans* isomerizations around the N=N bond were observed and characterized for the chromophores.

Introduction

Heterocycles play a prominent role in modern chemistry: They are important building blocks in supramolecular chemistry,[1] in biomimetic compounds for advanced pharmaceutical/medical applications[2] and in advanced materials, such as conducting polymers,[3] OFETs,[4] organic solar cells[5] and materials that exhibit non-linear optical (NLO) response.

The emergence of photonic technologies in telecommunications has led to a growing demand for NLO materials.[6] In this field, organic compounds are technologically privileged in principle, compared with inorganics because they exhibit large non-linearities with ultra-fast responses, and their ease of handling makes possible their integration with existing silicon-based technology.[6]

NLO effects depend on the ability of the molecular electronic cloud to show an electric-field-dependent polarizability. Accordingly, attention has been mainly focused on organic compounds possessing long conjugated domains (comprising polyene/phenylene backbones) end-capped with electron-donor and -acceptor groups to induce the necessary directional bias, the so-called push–pull chromophores.[6] Phenylene-based chromophores usually exhibit high electronic excitation energies, which, according to the well-known two-state model,[7] lowers the second-order NLO response. A simple way to obviate this shortcoming is to substitute phenylene with heteroaromatic rings due to the smaller aromatic stabilization energy of the heterocycle as compared with benzene. It has been experimentally shown that the presence of heterocycles significantly enhances the non-linear optical response of conjugated push–pull chromophores.[8]

The most studied chromophores contain single-ring aromatic heterocycles with one or more heteroatoms (e.g., pyridine,[9] pyrrole,[10] thiophene,[11] imidazole,[12] thiazole,[13] and oxadiazole[14]). Examples of chromophores containing two aromatic fused rings, one pentatomic heterocycle and one hexatomic non-heterocycle, have also been reported (benzimidazole,[15] benzoxazole[16] and benzothiazole[17]). Chromophores containing two fused rings that are both heteroaromatic are more rare, in particular, those in which both rings are pentatomic.[18] In the search for new heteroaromatic compounds suitable for quadratic NLO applications we have started a general investigation of push–pull chromophores containing two fused rings that are both heteroaromatic.

In this paper we report a study of chromophores containing the fused *s*-triazolo[3,4-*b*]thiadiazole heterocycle (Scheme 1). This heterocycle has been investigated recently in biochemistry and has a diverse biological activity.[19] Some of its features suggest that this heterocycle is interesting as a building block for NLO-active chromophores. a) The high number of electronegative nitrogen atoms and the sulfur atom are expected to increase the quadratic molecular NLO response[8] and to provide the whole chromo-

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[a] Department of Chemistry "Paolo Corradini",
University of Naples "Federico II",
Via Cinthia, 80126 Naples, Italy
[b] Department of Chemistry, University of Salerno,
Via S. Allende, 84081 Salerno, Italy
[c] Department of Chemistry-Physical Chemistry,
Technische Universität Kaiserslautern,
Erwin-Schrödinger Str., 67663 Kaiserslautern, Germany

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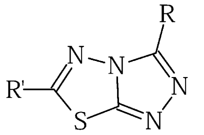
phore with a high dipole moment, which is another important requirement for obtaining acentric polar materials by the poling process. b) The planar geometry of the two fused rings allows good π-electron conjugation. c) The bent geometry of the bonds in the 2- and 5-positions is expected to confer on the chromophore a more oblate ellipsoid shape than prolate which, again, is reported to improve poling performances and hence NLO properties.[20]



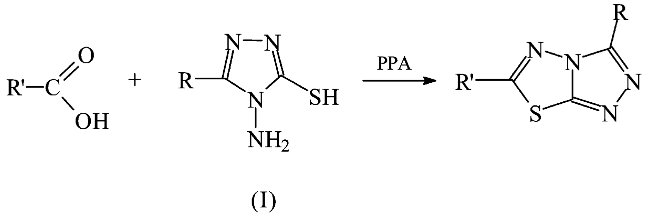
Scheme 1. Structure of the *s*-triazolo[3,4-*b*]thiadiazole heterocycle.

In a recent paper we reported the synthesis of a chromophore containing the heterocycle of Scheme 1 (with an additional electron-poor pyridine ring attached to the fused system at the 5-position) and some derived polymers.[21] In this report we describe the synthesis and full physicochemical characterization, including NLO measurements, of three new chromophores containing this heterocycle in which more powerful electron-acceptor groups have been introduced, for example, 4-nitrophenyl and 4-pentafluorophenyl. Moreover, the effect of introducing the acceptor onto the triazole or thiadiazole ring has also been investigated. The structures of the new chromophores are reported in Scheme 2 together with the structure of the previously reported chromophore **3**.

The chromophores were synthesized with two hydroxy groups to allow their use as monomers in polymerization reactions. The properties of the polymers will be reported in a separate publication.

Results and Discussion

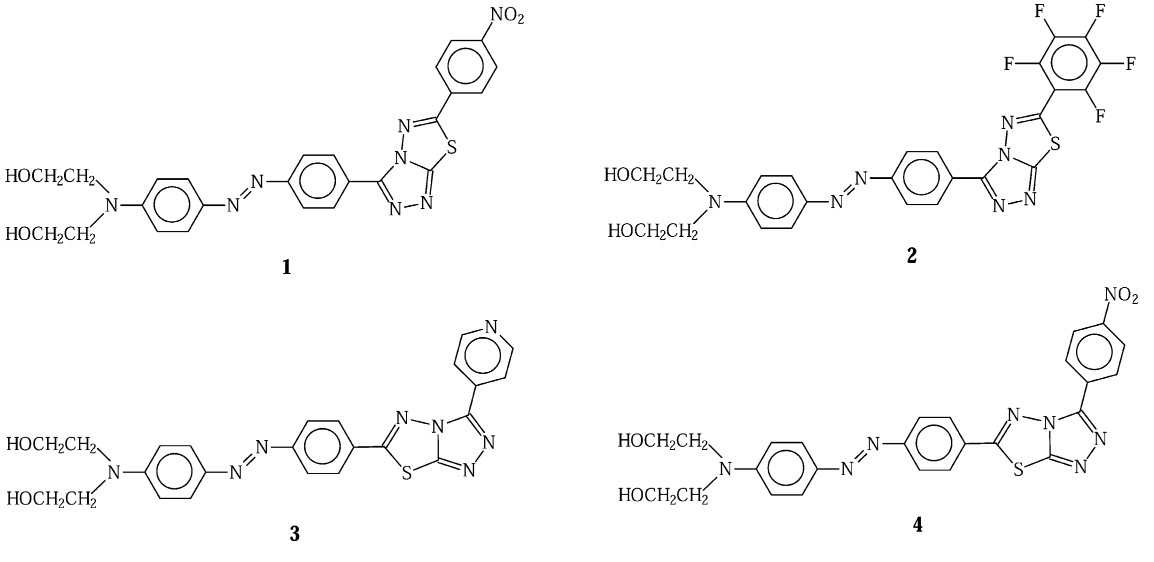
A versatile synthetic route to the *s*-triazolo[3,4-*b*]thiadiazole heterocycle is reported in Scheme 3; it is based on the cyclization between the 4-aminotriazole-3-thiol **I** and a carboxylic acid in the presence of a dehydrating agent, for example, polyphosphoric acid (PPA).[19c]



Scheme 3. Synthesis of the *s*-triazolo[3,4-*b*]thiadiazole heterocycle.

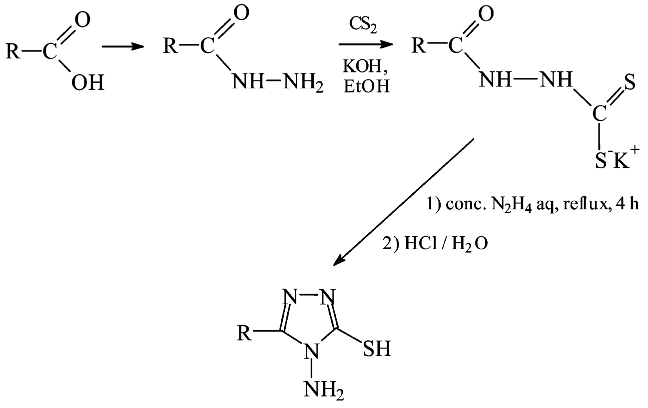
A general synthesis of the 4-aminotriazole-3-thiol **I** has been described by Hoggarth[22] and is shown in Scheme 4. The carboxylic acid RCOOH is converted (by standard methods) into the hydrazide, which is treated with carbon disulfide and KOH in absolute ethanol to afford the dithiocarbazate potassium salt. This is converted into the 4-aminotriazole-3-thiol in the final step by hydrazinolysis with elimination of H_2O and H_2S.

In summary, to synthesize the s-triazolo[3,4-*b*]thiadiazole heterocycle (Scheme 1), carboxylic acids RCOOH and R′COOH, hydrazine and CS_2 are needed as starting materials. The general route depicted in Schemes 3 and 4, and, in particular, the hydrazinolysis step of Scheme 4, is clearly inadequate if oxidizing groups are present in the molecule, for example, a nitro group. Because the nitro group is strongly electron-withdrawing it is widely used in push–pull NLO active compounds and therefore it is important to develop synthetic routes compatible with the presence of this



1 **2** **3** **4**

Scheme 2. Structures of the synthesized chromophores.



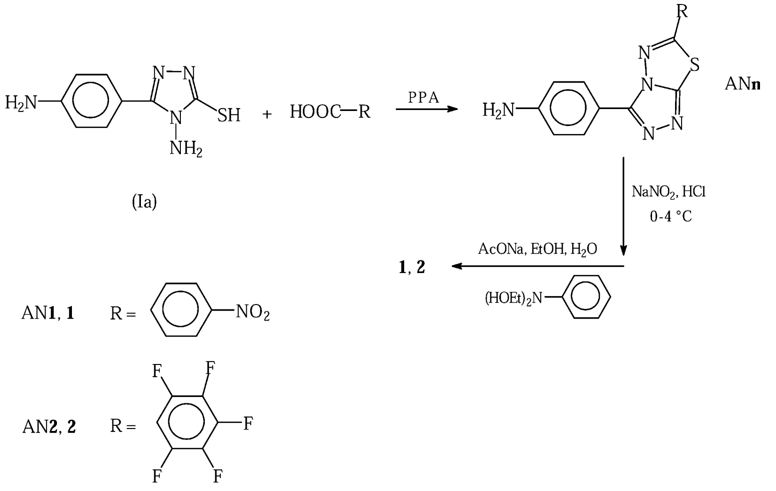
Scheme 4. Synthesis of the 4-amino-1,2,4-triazole-3-thiols.

group. In fact, the oxidizing nature of the nitro group has been exploited (starting from nitrobenzoic acid and following Scheme 4) to achieve, in a single hydrazinolysis step, ring-closure and reduction of the nitro to the amino group, so obtaining 4-amino-5-(4-aminophenyl)-1,2,4-triazole-3-thiol (**Ia**), which is the key intermediate in the synthesis of aniline precursors AN**1** and AN**2** and of chromophores **1** and **2**, as shown in Scheme 5. We note that in **1** and **2** the electron-withdrawing group is attached to the fused heterocycle through the thiadiazole ring.

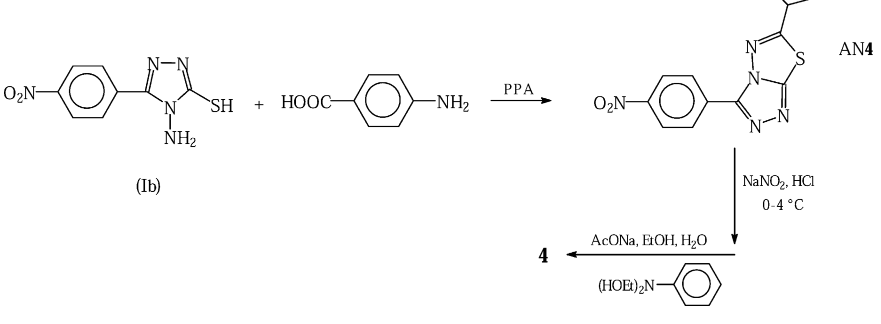
Chromophore **4** can be synthesized in a similar way by using *p*-aminobenzoic acid in the cyclization step provided the intermediate, 4-amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol (**Ib**), is available (Scheme 6). However, **Ib** cannot be obtained by the route shown in Scheme 4 because of reduction of the nitro group during the hydrazinolysis step. Thus, a different synthetic path was followed (Scheme 7).

The dithiocarbazate salt was converted into the oxadiazole derivative, 2-(4-nitrophenyl)-1,3,4-oxadiazole-5-thiol, by heating it at reflux in pyridine with the evolution of hydrogen sulfide.[22] After several trials with different concentrations of hydrazine, we found that the oxadiazole can be converted into the triazole **Ib** by reaction with suitably dilute hydrazine solutions. In this way, **Ib** was obtained in satisfactory yield and purity provided the molar concentration of hydrazine in the reaction solution was not more than 0.4 mol/L.

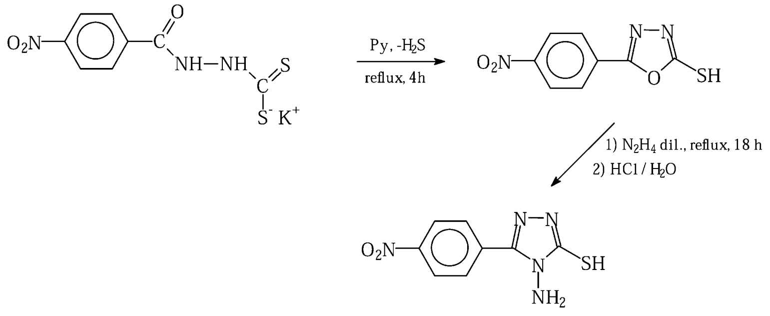
Some physicochemical properties of **1**–**4** are reported in Table 1. All chromophores show fair thermal stability, which is an important parameter for second-order NLO



Scheme 5. Synthesis of chromophores **1** and **2**.



Scheme 6. Synthesis of chromophore **4**.



(Ib)

Scheme 7. Synthesis of 4-amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol.

materials. The UV/Vis spectroscopic characterization data are similar for chromophores **1** and **2** and for **3** and **4**. For **3** and **4** the λ_{max} values are significantly redshifted compared with **1** and **2** (Figure 1).

Table 1. Physicochemical properties of the chromophores **1**–**4**.

	T_d [°C][a]	λ_{max} [nm][b]
1	277	469
2	280	468
3[c]	309	489
4	299	489

[a] Decomposition temperature corresponding to 5% weight loss. [b] Measured in DMF solution. [c] Data for **3** are taken from ref.[21].

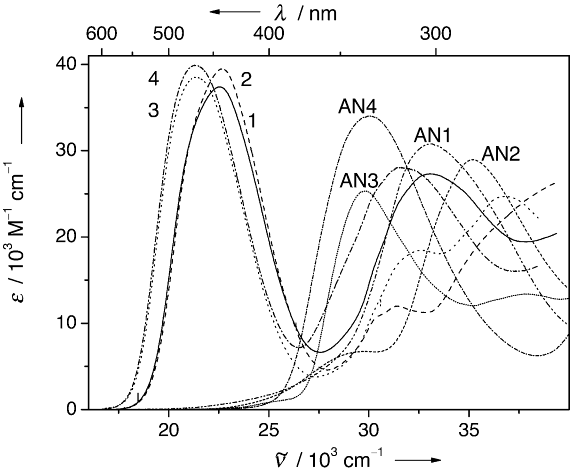


Figure 1. Absorption spectra of **1** (–), **2** (---), **3** (···), **4** (-·-·-), AN**1** (-··-··), AN**2** (----), AN**3** (···) and AN**4** (-·-·-) in 1,4-dioxane at T = 298 K after reaching equilibrium in the dark. The data for AN**3** and **3** are taken from ref.[21].

As depicted in Figure 1, the λ_{max} values of the precursors AN***n*** (***n*** = 1, 2, 3, 4) show the same behaviour and thus the gap between the first excited state of the ***n*** and AN***n*** compounds is approximately constant. Although the UV/Vis spectra of the AN***n*** compounds do not change with time after dissolving, the absorbance of the ***n*** compounds, after quickly dissolving the chromophores in daylight, increases with time upon storing in the dark as a result of a first or pseudo-first order reaction (Figure 2) with $k = 6.6(2) \times 10^{-4}\ s^{-1}$ in DMF and $2.9(1) \times 10^{-4}\ s^{-1}$ in 1,4-dioxane for **2**. For the other chromophores in 1,4-dioxane the following rate constants were found: $k > 1.7\ s^{-1}$ for **1**, $k = 1.00(1) \times 10^{-3}\ s^{-1}$ for **3** and $k = 1.7(3) \times 10^{-4}\ s^{-1}$ for **4**. Three clear isosbestic points show that only two different species take part in a reversible process (Figure 3). Irradiation with short-wavelength UV light reduces reversibly the absorption intensity through the backward reaction, which is at least one order of magnitude faster. This behaviour is compatible with the hypothesis that a *cis* → *trans* isomerization around the N=N bond occurs in the dark after the *trans* → *cis* reaction has been photochemically induced.[23] The molecular properties were all measured under equilibrium conditions in the dark; to evaluate the molecular properties the existence of 100% of the *trans* isomer has been assumed because the concentration of the *cis* form is at least one order of magnitude smaller, as can be estimated from the faster backward reaction.

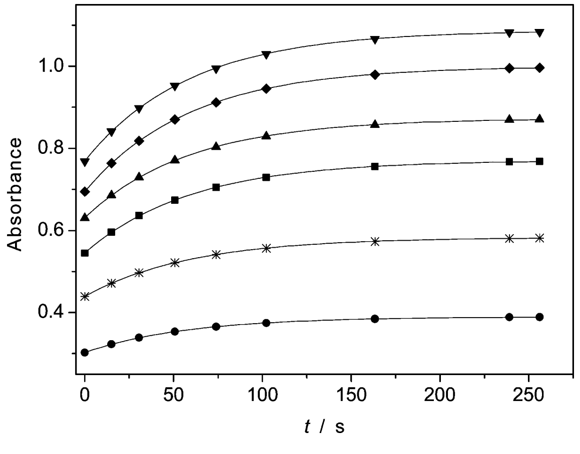


Figure 2. Time-dependent absorbances at different wavelengths: 500 (●), 475 (▲), 450 (▼), 425 (♦), 410 (■) and 400 nm (∗) for **2** measured in 1,4-dioxane at 298 K in the dark and the regression analysis (–) of the experimentally measured absorptions (the time-dependence of the EOA spectra shows the same results within experimental error with the same reaction rate).

The quadratic NLO activities of the chromophores **1**, **2** and **4** were measured by the EFISH technique. The results reported in Table 2 suggest that the substitution pattern

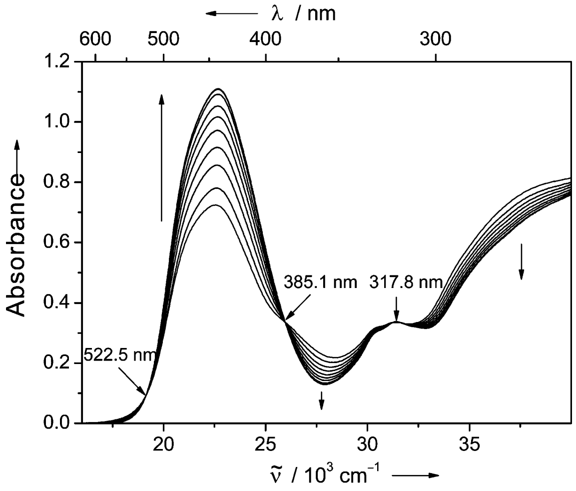


Figure 3. Increase of the absorption of **2** in 1,4-dioxane at T = 298 K in the dark over a period of 305 min. There are at least three isosbestic points, which indicates the existence of two different absorbing species.

with the electron-withdrawing group on the triazole ring (**4**) gives the highest NLO activity.

Table 2. EFISH data of the chromophores **1**, **2** and **4**.

	$\underline{\mu}_g \cdot \underline{\beta}$[a]	$\underline{\mu}_g \cdot \underline{\beta}_0$[b]
1	430	306
2	270	186
4[c]	980	675

[a] Measured by the EFISH technique at 1.9 μm in DMF at 298 K and expressed in 10^{-48} esu according to the phenomenological convention (X convention).[24] [b] Extrapolated to zero frequency using the two-level model. [c] Measured on the diacetylated derivative in chloroform at T = 298 K. The data are not solvent-corrected.

However, EFISH data include both the non-linear property of the molecule (in the form of $\underline{\beta}$, which is one of the vector parts of the $\underline{\underline{\beta}}$ tensor) and the ground-state dipole moment through their dot product. Thus we have carried out electro-optical absorption (EOA) measurements[25] and parallel DFT calculations to extract the important linear and non-linear chromophore properties (Tables 3 and 4). For easy comparison, we have also included in Table 3 EOA data for the chromophore **3** already published by us.[21]

The most striking feature of the EOA measurements is the difference in the ground-state dipole moments depending on the substitution pattern on the heterobicycle. In particular, if the electron-withdrawing group is on the triazole ring (**3**, **4**), the dipole moment is more than two times larger than if it is on the thiadiazole ring (**1**, **2**), a result that is qualitatively also found in DFT calculations. Thus, the higher EFISH response of **4**, as compared with the isomeric molecule **1**, is due more to the higher dipole moment of **4** than to a higher $\underline{\underline{\beta}}$. This trend in the experimental EFISH data is correctly reproduced both by the EOA measurements and by DFT results. In particular, the somewhat lower values obtained by EOA as compared with EFISH (Tables 2 and 3) probably results from the fact that in our experiments EOA spectroscopy only takes into account the contribution of the long-wavelength transition to $\underline{\underline{\beta}}$. The UV spectra reported in Figure 1 indicate that contributions from other bands in the shorter wavelength region may also be important. The spectroscopic data in Table 3 show also that the λ_{eg} values change according to the variation of the substitution pattern: with the electron-withdrawing group on the thiadiazole ring the values of λ_{eg} are about 20 nm shorter and this, too, is consistent with the DFT analysis (Table 4). On the other hand, the experimental results of the EFISH and EOA measurements in comparison with the DFT calculations refer to different situations and thus the quantitative correlation is less satisfactory. This can be explained by the fact that in the DFT calculations we have considered only optimized geometries. A few test computations indicate that there are other low-energy conformers involving either different conformations of the HO-alkyl tails and torsions within the conjugated systems (which are fully planar in the optimized geometries) with dipole moments lower also by 3–4 D Thus, a statistical average appears to be necessary for a more significant comparison between the experimental and theoretical data of these chromophores. In solution, in fact, a distribution of conformers exists and the EOA and EFISH methods measure the mean, which leads to a smaller $\underline{\mu}_g$ and thus to a smaller $\underline{\mu}_g \cdot \underline{\beta}_0$.

Thus, by comparing the DFT with EOA data it can be noted that DFT overestimates ground-state dipole moments and underestimates $\underline{\beta}_0$ values in such a way that DFT-calculated values of $\underline{\mu}_g \cdot \underline{\beta}_0$ do follow the trends shown by experi-

Table 3. EOA data of the chromophores **1**–**4**.

	λ_{eg} [nm][a]	μ_{eg} [D][a]	β_0 [10^{-30} esu]	μ_g [D][b]	$\Delta\mu$ [D]	$\underline{\mu}_g \cdot \underline{\beta}_0$ [10^{-48} esu][c]
1	444.2	8.8	73	3.4	13.1	234
2	441.1	8.9	103[d]	3.6	21.7	195
3	467.5	8.9	93	8.5	14.2	766
4	469.6	9.1	105	9.4	15.6	888

[a] Data refer to measurements in 1,4-dioxane; all other data are measured in 1,4-dioxane and then corrected for the gas phase. [b] Solvent corrections were made using the Onsager factor f for spherical particles. This approximation is to some extent responsible for the discrepancies between experimental and theoretical results due to the elongated and flat shape of the molecules. [c] In accord with the phenomenological convention (X convention). [d] Overestimated by the applied equation of the two-state model because of the large angle between $\underline{\mu}_g$ and the corresponding $\underline{\mu}_{eg}$.

Table 4. NLO data claculated for chromophores **1**–**4**.

	λ_{eg} [nm]	μ_{eg} [D]	μ_g [D]	β_{0par} [10^{-30} esu][a]	$\lvert\underline{\mu}_g \cdot \underline{\beta}_0\rvert$ [10^{-48} esu]	$\angle(\underline{\mu}_g,\underline{\beta}_0)$ [°]
1	431	10.7	7.7	56	434	19
2	421	11.2	8.0	31	245	34
3	454	11.6	14.9	62	927	9
4	467	10.4	16.5	75	1236	11

[a] In accord with the phenomenological convention (X convention).

mental EFISH and EOA measurements. It can also be pointed out that, with the only exception of **2**, the trend in the DFT-calculated $\underline{\beta}_0$ values is in agreement with EOA data. Concerning, in particular, the evaluation of the hyperpolarizabilities $\underline{\beta}_0$ by EOA spectroscopy, it should be remembered that collinearity of the CT transition moment and ground-state dipole moment vectors ($\underline{\mu}_{eg}$ and $\underline{\mu}_g$), as well as of the $\underline{\beta}$ and $\underline{\mu}_g$ vectors, has been used here as an approximation. This assumption is strictly true only for linear chromophores, whereas the chromophores investigated, and in particular **1** and **2**, have a bent shape, which allows the existence of transition and dipole moments that are not parallel to each other. The apparent anomaly of **2** can be explained, at least in part, by the larger angle between the $\underline{\beta}_0$ and $\underline{\mu}_g$ vectors (Table 4).

A careful analysis of the results of the DFT calculations and the EOA spectra allows the following conclusions to be drawn concerning the different properties of the chromophores in relation to the substitution pattern on the heterobicycle. The transition moment of the CT transition ($\underline{\mu}_{eg}$) is approximately parallel to the long axis of the diazobenzene subunit for all the chromophores. The angle between $\Delta\underline{\mu} = \underline{\mu}_e - \underline{\mu}_g$ and $\underline{\mu}_g$, however, is larger for **2** (**1**) and smaller for **4** (**3**) (Figure 4). Furthermore, the different orientation of the heterobicycle relative to its polar substituent causes differently oriented dipole moments in the ground and excited states for **2** (**1**) and **4** (**3**). This different orientation is responsible for the different interaction of the two local chromophores, the diazo group and the heterocycle. The enlargement of the conjugation length in **4** (**3**) leads, in comparison with **2** (**1**), to an enhancement of the absorption intensity and to a shift of the absorption maxima. This leads to an essential difference between these two classes of molecules. Whereas in **4** (**3**) the total intensity of the CT band contributes to the vector $\underline{\beta}_0$ and thus to $\underline{\mu}_g{\cdot}\underline{\beta}_0$, for **2** (**1**) the contribution is reduced because of the larger angle between the transition moment and the orientation axis of the heterocycle due to the greater bending in these molecules (Figure 4). For **2** (**1**) the CT band contributes only in part to $\underline{\mu}_g{\cdot}\underline{\beta}_0$ and the vector $\underline{\beta}_0$ is oriented differently with respect to the molecular frame compared with **4** (**3**). Thus, chromophores with bent structures can be suitable for quadratic NLO applications,[20] but only if the bending does not introduce moments that are oblique to each other and this effect dominates.

Conclusions

A family of quadratically NLO-active azo-chromophores containing the 10-electron heterocycle *s*-triazolo[3,4-*b*]thiadiazole has been prepared. Synthetic strategies allowing the substitution of an electron-withdrawing group (nitrophenyl) on the triazole or thiadiazole ring have successfully been developed. EFISH and EOA measurements as well as DFT calculations have shown that different substitution patterns on the heterobicycle strongly affect the linear and nonlinear electronic properties, in particular, the ground-state electric dipole moment. Both the theoretical calculations and EOA results conform with EFISH in their relative degree of NLO properties within the series of compounds.

Experimental Section

Potassium 2-(4-Nitrobenzoyl)hydrazinecarbodithioate: Potassium hydroxide (6.615 g, 117.9 mmol), 4-nitrobenzoic acid hydrazide (12 g, 66.2 mmol) and absolute ethanol (132 mL) were stirred at room temperature under N_2 in a round-bottomed flask equipped with a condenser. Carbon disulfide (12 mL, 200 mmol) was then added. An orange solid immediately formed and absolute ethanol (97 mL) was added. After stirring for 1 h, further carbon disulfide was added (same quantity as the initial addition) and the mixture was allowed to stir overnight at room temperature. The orange solid was filtered, washed with cold absolute ethanol and dried in vacuo at 70 °C; yield 16.12 g (88%); m.p. 155 °C (dec.). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 8.07 (d, J = 8.4 Hz, 2 H), 8.28 (d, J = 8.6 Hz, 2 H), 9.77 (s, 1 H), 10.64 (s, 1 H) ppm.

4-Amino-5-(4-aminophenyl)-1,2,4-triazole-3-thiol (Ia): Potassium 2-(4-nitrobenzoyl)hydrazinecarbodithioate (21.21 g, 71.81 mmol) was suspended in ethanol (106 mL) and hydrazine monohydrate (37.2 mL) was added. The solution obtained was heated at reflux for 5 h. The initial red solution turned green and evolution of gas was observed (H_2S, according to the lead acetate paper test). After 5 h at reflux, the solution was poured into cold water (100 mL) acidified at pH = 5 with 37% HCl to yield 23.83 g of a white solid; m.p. 265 °C; yield 5.953 g (40%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ = 5.54 (s, 2 H), 6.41 (m, 2 H), 7.51 (m, 2 H), 13.42 (s, 1 H) ppm.

2-(4-Nitrophenyl)-5-(4-aminophenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (AN1): A mixture containing **Ia** (4.000 g, 19.30 mmol), *p*-nitrobenzoic acid (3.225 g, 19.30 mol) and polyphosphoric acid (PPA; ca. 102 g) was heated whilst stirring. The temperature of the mixture was gradually increased from 100 to 200 °C over 20 min to give a brown paste. The reaction was continued for 5 h. Then, the

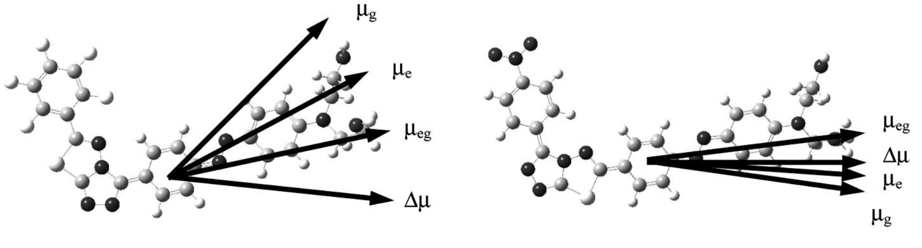


Figure 4. Relative orientations of the ground- and excited-state dipole moments, transition moments and dipole moment differences for **2** (left) and **4** (right). All vectors have been normalized.

brown paste was poured into water and ice (200 mL) and formed a yellow solid. By increasing the pH of the suspension up to 5 using an aqueous NaOH solution, the colour of the suspension turned from yellow to brown. The brown solid was recovered by filtration and washed with 10 wt.-% aqueous Na_2CO_3. After filtration and abundant washing with water, a brown crystalline solid was collected and dried in an oven at 120 °C for 4 h; yield 5.420 g (83%); m.p. 250 °C. ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 5.73 (s, 2 H), 6.69 (d, J = 8.4 Hz, 2 H), 7.92 (d, J = 8.6 Hz, 2 H), 8.22 (d, J = 8.8 Hz, 2 H), 8.35 (d, J = 8.8 Hz, 2 H) ppm.

2-(2,3,4,5,6-Pentafluorophenyl)-5-(4-aminophenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (AN2): This compound was obtained by the same synthetic procedure used for the preceding compound but using pentafluorobenzoic acid instead of 4-nitrobenzoic acid. Moreover, the reaction mixture was initially held at 150 °C for 1 h before further increasing the temperature to avoid sublimation of the acid; yield 70%; m.p. 280 °C (dec). ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 5.71 (s, 2 H), 6.63 (d, J = 8.2 Hz, 2 H), 7.82 (d, J = 8.8 Hz, 2 H) ppm.

2–(4-Nitrophenyl)-5-(4-{4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenylazo}phenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (1): For the synthesis of **1** and **2** the same synthetic procedure was adopted: AN1 (3.000 g, 8.867 mmol) was suspended in water (20 mL) whilst stirring at 0–4 °C. A 37% solution of HCl (4.6 mL) was added. Sodium nitrite (0.667 g, 9.67 mol), dissolved in the minimum amount of water, was added dropwise to the mixture. The addition of nitrite caused the suspension to become dark. After 40 min after the last addition of nitrite, the suspension containing the diazonium salt was poured into an aqueous solution (100 mL) containing anhydrous sodium acetate (5.000 g) and *N*,*N*-bis(2-hydroxyethyl)aniline (1.607 g, 8.867 mmol). A dark-red precipitate was obtained immediately. After stirring for 1 h at room temperature, the solid was filtered and recrystallized from DMF/H_2O to give **1** as a dark-red microcrystalline solid; m.p. 277 °C (dec.); yield 2.164 g (46%). ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 3.57 (s, 8 H), 4.85 (m, 2 H), 6.80 (d, J = 8.0 Hz, 2 H), 7.70 (d, J = 8.8 Hz, 2 H), 7.86 (d, J = 8.6 Hz, 2 H), 8.24–8.40 (m, 6 H) ppm. $C_{25}H_{22}N_8O_4S$ (530.568): calcd. C 56.59, H 4.18, N 21.12; found C 56.36, H 4.29, N 20.95.

2–(2,3,4,5,6-Pentafluorophenyl)-5-(4-{4-[*N*,*N*-bis(2-hydroxyethyl)amino]phenylazo}phenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (2): The compound obtained in this case was a red microcrystalline solid that decomposes at about 280 °C. The yield was the same as for **1**. ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 3.57 (s, 8 H), 4.82 (m, 2 H), 6.83 (d, J = 8.8 Hz, 2 H), 7.73 (d, J = 8.8 Hz, 2 H), 7.89 (d, J = 8.8 Hz, 2 H), 8.29 (d, J = 8.2 Hz, 2 H) ppm. $C_{25}H_{18}N_7O_2F_5S$ (575.521): calcd. C 52.17, H 3.15, N 17.04; found C 52.32, H 3.37, N 17.08.

4-Amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol (NO_2-triazole)

Step 1. Synthesis of 2-(4-Nitrophenyl)-1,3,4-oxadiazole-5-thiol: Potassium 2-(4-nitrobenzoyl)hydrazinecarbodithioate (8.110 g, 27.46 mmol) and pyridine (52 mL) were heated at reflux for 4 h. The suspension containing an orange solid was then poured into water (73 mL) and a white solid formed. This was filtered and the mother liquor acidified with a 37% HCl solution until pH = 4. The yellow solid formed was collected and recrystallized from ethanol/water to give yellow needle-shaped crystals; m.p. 207 °C (dec.); yield 4.107 g (67%). ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 8.00 (d, J = 7.7 Hz, 2 H), 8.22 (d, J = 8.7 Hz, 2 H), 14.02 (br. s, 1 H) ppm.

Step 2. 4-Amino-5-(4-nitrophenyl)-1,2,4-triazole-3-thiol (Ib): 2-(4-Nitrophenyl)-1,3,4-oxadiazole-5-thiol (2.001 g, 8.960 mmol) and 150 mL of a solution obtained by mixing hydrazine monohydrate (7.2 mL, 148.4 mmol) and water (391 mL) were heated at reflux in a round-bottomed flask. After 10 h, a further 150 mL of the same hydrazine/water solution was added and the mixture was heated at reflux for 4 h. After this period the remaining hydrazine/water solution was added and the reaction mixture heated at reflux for 4 h. Then the reaction solution was acidified at pH = 4 with a 37% HCl solution. The yellow solid obtained was filtered, washed with cold water and dried in an oven; m.p. 182 °C; yield 0.978 g (46%). ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 5.84 (s, 2 H), 8.34 (m, 4 H), 14.16 (s, 1 H) ppm.

2-(4-Aminophenyl)-5-(4-nitrophenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (AN4): Ib (0.900 g, 3.794 mmol), 4-aminobenzoic acid (0.520 g, 3.794 mol) and ca. 30 g of PPA were allowed to react for 4 h at 200 °C, increasing gradually the temperature from 100 to 200 °C over 20 min. After 4 h of reaction, the green paste obtained was poured into a mixture of water and ice (100 mL). A green-yellow solid formed. On addition of aqueous NaOH up to pH = 5, the solid changed from green-yellow to orange. After filtering and washing with 10 wt-.% aqueous sodium carbonate a dark-orange solid was finally collected; m.p. 249 °C (dec.); yield 1.053 g (82%). ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 6.25 (s, 2 H), 6.66 (d, J = 8.8 Hz, 2 H), 7.67 (s, J = 8.8 Hz, 2 H), 8.37 (dd, 4 H) ppm.

2-(4-{4-[*N*,*N*-Bis(2-hydroxyethyl)amino]phenylazo}phenyl)-5-(4-nitrophenyl)[1,2,4]triazolo[3,4-*b*][1,3,4]thiadiazole (4): The synthetic procedure involves a diazotization/coupling strategy analogous to that used for **1** and **2**; m.p. 299 °C (dec); yield 55%. ^1H NMR (300 MHz, $[D_6]$DMSO, 25 °C): δ = 3.46 (m, 8 H), 4.70 (br. s, 2 H), 6.70 (d, J = 8.7 Hz, 2 H), 7.63 (d, J = 7.8 Hz, 2 H), 7.76 (d, J = 8.4 Hz, 2 H), 8.02 (d, J = 7.8 Hz, 2 H), 8.29 (d, J = 8.7 Hz, 2 H), 8.41 (d, J = 8.1 Hz, 2 H) ppm. $C_{25}H_{22}N_8O_4S$ (530.568): calcd. C 56.59, H 4.18, N 21.12; found C 56.40, H 4.34, N 20.87%.

Physical Measurements: The thermal behaviour of the synthesized compounds was studied by DSC (Perkin–Elmer Pyris, scanning rate 10 °C/min, nitrogen flow), optical observations (Zeiss Axioscop polarizing microscope, Mettler FP90 heating stage) and thermogravimetric analysis (Mettler TG50, air atmosphere). ^1H NMR spectra were recorded with Varian and Gemini spectrometers operating at 200 or 300 MHz.

The conventional EFISH technique was used to determine experimentally the non-linearity $\underline{\mu}_g \cdot \underline{\beta}_0$ of the chromophores, where $\underline{\mu}_g$ is the ground-state permanent dipole moment of a molecule and $\underline{\beta}$ is the vector part of the quadratic hyperpolarizability tensor of a molecule. The light source was a Q-switched Nd:Yag laser the emission of which at 1.06 µm was shifted to 1.907 µm by stimulated Raman scattering in a high-pressure hydrogen cell. The measurements were calibrated relative to a quartz wedge: the experimental value of $d_{11}^{\mathrm{Quartd}} = 1.2 \times 10^{-9}$ esu at 1.06 µm was extrapolated to 1.11×10^{-9} esu at 1.907 µm. Measurements were performed neglecting the electric field dependence of molecular properties and allowing for Kleinman symmetry.[26] Measurements were performed in DMF solution for **1** and **2** and in chloroform solution for the diacetylated derivative of **4**. The results given in the text are in accord with the phenomenological convention (X convention).[24]

Dipole moments of the ground state μ_g and the dipole moment differences $\Delta\mu = \mu_e - \mu_g$ (μ_e is the excited-state dipole moment) of the chromophores were determined by electro-optical absorption (EOA) spectroscopy by which the difference of absorption of a solution with $[\varepsilon^E(\phi,\nu)]$ and without $[\varepsilon(\nu)]$ an external applied electric field $\underline{E}$ is measured with light polarized parallel ($\phi = 0°$) and perpendicular (ϕ = 90°) to the direction of **E**.[27] For uniaxial phases, induced in a solution by both an alternating and a constant electric field of about 3×10^6 V m^{-1}, the dichroism $\varepsilon^E(\phi,\nu) - \varepsilon(\nu)$ depends on the orientational order of the molecules due to their ground-state dipole moment μ_g, the shift of the absorption band proportional to the dipole moment difference $\Delta\mu$ and the electric-field dependence of the electric-transition dipole moment $\mu_{eg}(E)$. UV/Vis spectra, required for the evaluation of the integral absorption ($\propto \mu_{eg}^2$), were recorded with a Perkin–Elmer Lambda 900 spectrophotometer at 298 K.

Theoretical Calculations: Dipole moments and static first-order hyperpolarizabilities were computed by using density functional theory with the hybrid B3LYP exchange correlation potential[28] and the standard 6-31G** basis set. Several tests have shown that the use of a larger basis set and different exchange correlation potentials does not increase significantly the accuracy of the computed quantities. The minimum energy nuclear configurations were obtained by full geometry optimization at the same level of computation; the finite field procedure was used to calculate first-order hyperpolarizability. All computations were performed using the Gaussian03 package of software.[29] The applicability of the hybrid density functional theory methods to the calculation of molecular hyperpolarizability has sometimes been questioned[30] because it overestimates $\underline{\beta}$. However, that conclusion was mainly achieved by comparison with different computational methods rather than with experimental data. As concerns the computation of dipole moments, it has been shown that hybrid DFT computations with the same basis set used in this paper systematically overestimate dipole moments of organic dyes with electron-donor and-acceptor groups by an average factor of 1.4 with respect to experimental ones.[31] Notwithstanding these shortcomings, recent work has shown that this computational method is suitable, at least, for comparative purposes, for use with chromophores of similar structures.[32]

Supporting Information (see footnote on the first page of this article): Kinetic evaluation, EAO determination of linear and nonlinear optical properties, the electro-optical coefficients and calculated angles are presented.

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