Donor-Substituted Heptaazaphenalene as a Nonlinear Optically Active Molecule with Multiple Charge-Transfer Transitions[‡]

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The synthesis of a novel nonlinear optical (NLO) chromophore with threefold symmetry – 2,5,8-tris(diethylamino)-1,3,4,6,7,9,9b-heptaazaphenalene (**4**) – is reported. Compound **4** was synthesized from 2,5,8-trichloro-1,3,4,6,7,9,9b-heptaazaphenalene (**3**) through a nucleophilic aromatic substitution, its structural assignment was confirmed by X-ray investigations, and its second-order polarisability (β) was determined by hyper Rayleigh scattering (HRS). Compound **4** shows a very high absorbance coefficient in the UV and a remarkably large β value despite its short-wavelength absorption.

Introduction

Interest in organic substances as nonlinear optical materials is still topical owing to their advantages over inorganic materials.[1–7] While great progress has been made in the optimization of such one-dimensional (1D) NLO chromophores, it has become apparent that some problems in NLO cannot be effectively addressed by this approach. One is the efficiency/transparency trade-off, which is of crucial importance for second harmonic generation (SHG). The efficiency of the energy conversion must be high, but the reabsorption of the converted light low. However, the desirable increase in second-order polarisabilities in more extended π-systems is usually accompanied by a bathochromic shift of the CT transition.[6] Furthermore, the strong variation of the refractive index makes it difficult to achieve noncritical phase-matching between fundamental and frequency-doubled wave in a bulk material or crystal, and so alternative design strategies at the molecular level are desirable. One approach exploits the possibilities of π-systems with several donor and acceptor groups.[8] In addition, the search for new molecular structures and compounds with promising NLO properties is still necessary.

Here we present a new type of 2D NLO chromophore with D_{3h} symmetry, based on a central 1,4,6,7,9,9b-heptaazaphenalene moiety. This heterocyclic π-system represents an extended central acceptor group offering greater conjugation length and pronounced electron delocalization. The new system provides interesting β values at an improved efficiency/transparency ratio relative to *p*-nitroaniline (*p*NA), the prototype dipolar aromatic system.[9] Although the synthesis of the related 2,5,8-tris(cyanamino)-1,3,4,6,7,9,9b-heptaazaphenalene (**1**) has been known for a very long time,[10–12] the compound is still of considerable interest, as shown by current studies in materials science (such as its graphite-like behaviour),[13–14] as a building unit in polymers[15] and by photoelectron spectroscopic investigations.[16] Heptaazaphenalene can be regarded as an extension of the well characterized *s*-triazines, a class of compounds with NLO properties that compare very well with those of the best dipolar systems.[17] We therefore decided to test this analogy by studying the NLO properties and the structure of **4**.

Synthesis

The synthesis of cyameluric acid was published by Reedemann and Lucas in 1939.[18] Their procedure describes the treatment of sodium thiocyanate with chlorine in aqueous solution. This produced a red precipitate, which turned yellow when heated. The constitution of the product was assigned as 2,5,8-tris(cyanamino)-1,3,4,6,7,9,9b-heptaazaphenalene (**1**) (Scheme 1), named melon. Heating of melon at reflux with an aqueous solution of potassium hydroxide and workup with 6 N hydrochloric acid yielded cyameluric

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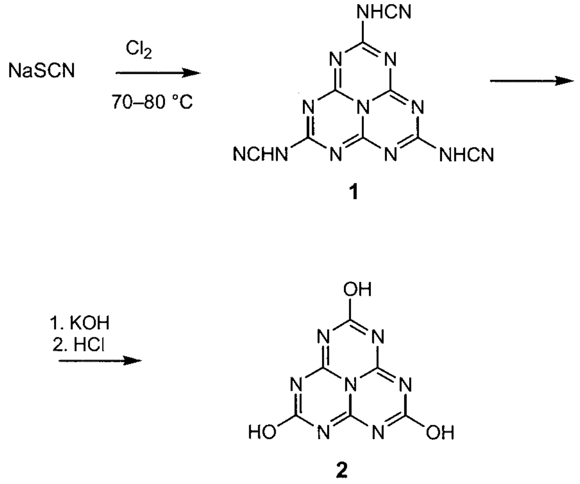
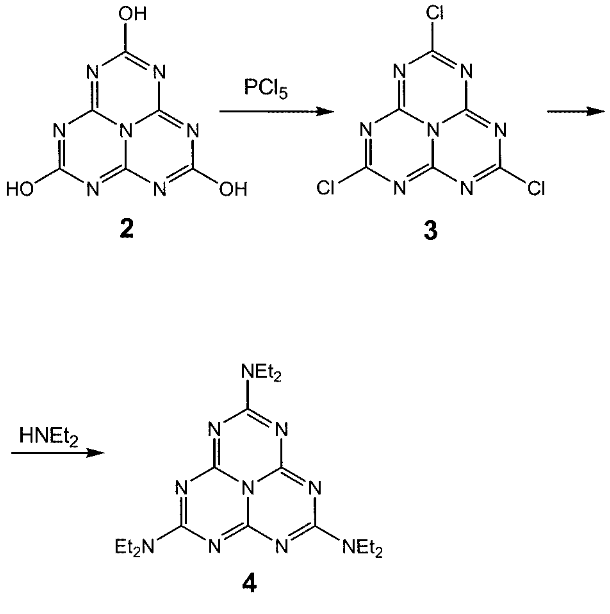
acid (**2**) as a white powder rather insoluble in common solvents.



Scheme 1

Cyameluric acid was converted into 2,5,8-trichloro-1,3,4,6,7,9,9b-heptaazaphenalene (**3**) by heating of **2** with PCl_5 in a bomb vessel at 220 °C for three days (Scheme 2).[19–20] The target molecule was then obtained by heating of **3** with diethylamine at 100 °C under pressure. The introduction of the diethylamino groups resulted in a good solubility of **4**, allowing its purification by column chromatography.



Scheme 2

Structural Investigations

We were able to grow single crystals of **4** by recrystallisation from hexane/CH_2Cl_2 solution. The molecular structure of **4** is shown in Figure 1, and shows the anticipated planar π-system. The peripheral C−N bond lengths vary between 1.32 and 1.36 Å, and the C−N distance involving the central nitrogen atom is 1.40 Å. The values obtained for the peripheral C−N bonds compare well with those reported in triazines.[21] The bond lengths of the external C−N bonds (1.34 Å) are somewhat shorter than those reported for other donor−acceptor systems such as 2,4,6-tris(4-diethylaminophenylethynyl)-1,3,5-triazine.[17]

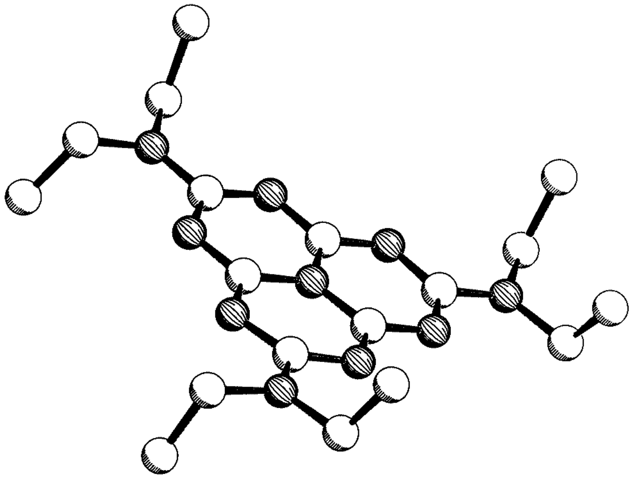


Figure 1. Molecular structure of **4**; hydrogen atoms are omitted; nitrogen atoms are hatched

Linear and Nonlinear Optical Properties

The UV/Vis spectrum of **4** in dioxane shows an intense band at 271 nm (ε = 93610 m^2/mol) and a shoulder at 248 nm (ε = 49780 m^2/mol). The oscillator strength of the long-wave absorption band is calculated to be *f* = 2.9. An emission band of **4** is observed at λ = 386 nm, indicating a large Stoke's shift. The spectrum reveals the very high absorption coefficient and complete transparency in the region of the second harmonic wavelength. The normalized absorption and emission spectra of **1** are displayed in Figure 2.

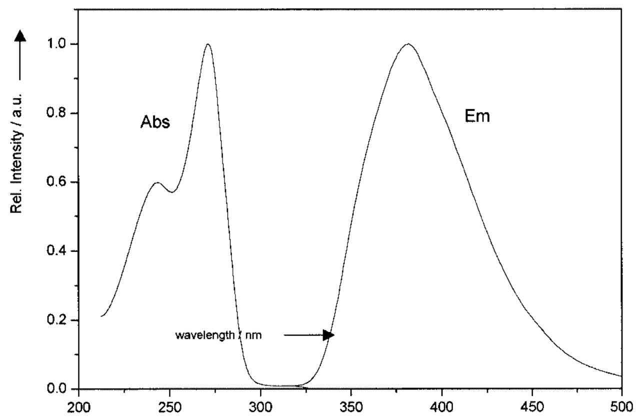


Figure 2. Absorption and emission spectra of **4** in dioxane solution at 298 K, corrected and standardised to 1 (Abs: absorption; Em: emission)

Because the 2D NLO chromophores of **4** (D_{3h} symmetry) have no dipole moment, it is not possible to determine their second-order polarisability by electric field-induced second harmonic generation (EFISHG). Instead, the hyper Rayleigh scattering (HRS) method, which does not rely on the dipolar alignment of the chromophores in an externally applied electric field, was applied. The HRS signal is generated by incoherent scattering caused by fluctuations of the second-order susceptibility of the solution. The measured values were compared with those of *p*NA (Figure 3).

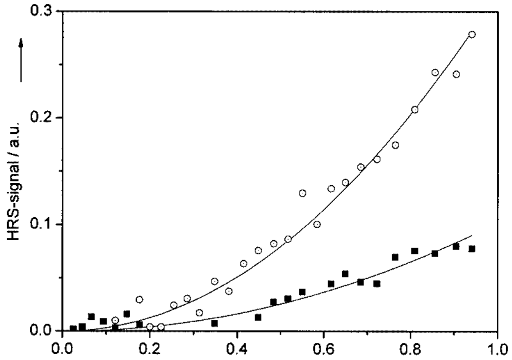


Figure 3. HRS measurements of *p*NA (open circles, c = 0.0848 mol/L) and **4** (solid squares, c = 0.0392 mol/L) in dioxane at T = 298 K

A laser polarised perpendicularly to the scatter plane was used, detection taking place at a parallel alignment of the analyser. The value for the β_{zzz}-component of the second-order polarizability tensor was determined by external reference to a *p*NA standard[22,23] to be $\beta_{zzz} = 18 \times 10^{-50}$ $C{\cdot}m^3{\cdot}V^{-2}$ (T convention; 10^{-50} $C{\cdot}m^3{\cdot}V^{-2} = 2.694 \times 10^{-30}$ esu).[6] The dispersion corrected value is $\beta^0_{zzz} = 12.5 \times 10^{-50}$ $C{\cdot}m^3{\cdot}V^{-2}$. Despite the very short conjugation length and its considerably blue-shifted absorption ($\lambda_{max.}$ = 271 nm) the nonlinearity of **4** compares very well with that of *p*NA ($\beta_{zzz} = 27 \times 10^{-50}$ $C{\cdot}m^3{\cdot}V^{-2}$, $\beta^0_{zzz} = 13.6 \times 10^{-50}$ $C{\cdot}m^3{\cdot}V^{-2}$, $\lambda_{max.}$ = 354 nm).[22] This and the high thermal stability make chromophores containing the heptaazaphenalene moiety attractive for NLO applications. The heptaazaphenalenee moiety may also be functionalized by one or two acceptor groups instead of donor groups, which should give rise to 2D NLO chromophores with C_{2v} symmetry and potential deviations of the second-order polarisability from Kleinman symmetry.[23] Such chromophores would also exhibit a resultant dipole moment that might be employable in electric field poled host−guest systems.

Conclusion

We have shown that a donor-substituted heptaazaphenalene derivative is accessible in a few steps from simple precursors. Its molecular structure reveals D_{3h} symmetry for the π system. The β_{zzz} values was determined by hyper-Rayleigh scattering (HRS). Compound **4** has been introduced as a novel nonlinear optical chromophore with excellent transparency/efficiency properties and a very high absorbance coefficient in the UV spectral region. The heptaazaphenalene unit represents a new, very strong acceptor group, promising for the design of new chromophores for second-order NLO applications.

Experimental Section

General: The diethylamine (Merck) was used without further purification. Melon, cyameluric acid and 2,5,8-trichloro-1,3,4,6,7,9,9b-heptaazaphenalene were synthesized by literature methods.[18] Melting points (Büchi B-540) are given uncorrected. NMR spectra: 300.133 MHz for ^1H, 75.469 MHz for ^{13}C. Microanalyses: University of Heidelberg, Analytical Laboratory.
HRS experiments were carried out at λ = 1064 nm in 1,4-dioxane (dried with sodium/potassium alloy and distilled prior to use) by a previously described procedure.[9,22] It was ensured that the HRS signals were not superimposed by spurious fluorescence. As an external standard, a 1 wt.-% solution of 4-nitroaniline (*p*NA) in 1,4-dioxane was used, assuming a value of $\beta_{zzz} = 27.4 \times 10^{-50}$ $C{\cdot}m^3{\cdot}V^{-2}$ for *p*NA as determined by EFISHG measurements.[23] Optical absorption spectra were recorded with a Perkin−Elmer Lambda 900 UV/Vis/NIR spectrometer. The temperature was adjusted to 298 K by use of a Lauda Ecoline 200 Thermostat. The spectra were recorded in 1-cm quartz cells.

2,5,8-Tris(diethylamino)-1,3,4,6,7,9,9b-heptaazaphenalene (4): 2,5,8-Trichloro-1,3,4,6,7,9,9b-heptaazaphenalene (**3**, 1.5 g, 5.4 mmol) and Et_2NH (37.5 mL) were sealed in a bomb vessel and heated at

Table 1. Crystallographic data of **4**

Empirical formula	$C_{18}H_{30}N_{10}$
Formula mass [g/mol]	386.52
Crystal size [mm]	0.6 × 0.1 × 0.1
Crystal colour	colourless
Crystal shape	needle
Space group	$P2_1/n$
a [Å]	17.8949(9)
b [Å]	4.7914(3)
c [Å]	23.845(2)
β [°]	101.147(2)
V [Å^3]	2005.9(2)
$D_{calcd.}$ [Mg/m^3]	1.28
Z	4
F(000)	832
T [K]	200
$h_{min.}/h_{max.}$	−22/23
$k_{min.}/k_{max.}$	−5/4
$l_{min.}/l_{max.}$	−31/31
Θ range [°]	2.6−28.0
μ [mm^{-1}]	0.08
Refl. collected	5188
Refl. unique	3387
Refl. observed [$I > 2\ \sigma\ (I)$]	2040
Variables	373
$(\Delta/\sigma)_{max.}$	0.001
R	0.050
R_w	0.104
S (Gof)	0.97
$(\Delta\rho)_{max.}$ [e·Å^{-3}]	0.18
$(\Delta\rho)_{min.}$ [e·Å^{-3}]	−0.26

100 °C for 3 d. The solution was filtered off and the solvent was evaporated. The residue was dissolved in ethyl acetate and washed with half concentrated brine and dried, and the solvents were evaporated. Column chromatography (SiO_2, ethyl acetate) yielded **4** (315 mg, 15%). White crystals, m.p. 218 °C. UV/Vis (CH_2Cl_2): λ (ε) = 248 (49781), 272 nm (90111). IR (KBr): $\tilde{\nu}$ = 2976, 2933, 2871, 1639, 1539, 1488, 1436, 1124, 807 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (*t*, ^3J = 7.1 Hz, 18 H), 3.67 (*t*, ^3J = 7.1 Hz, 12 H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.31, 41.17, 154.99, 162.38 ppm. MS (EI^+): *m*/*z* = 386 (43) [M^+], 371 (5) [$M^+ - CH_3$], 357 (100) [$M^+ - CH_3{-}CH_3$]. $C_{18}H_{30}N_{10}$ (386.50): calcd. C 55.94, H 7.82, N 36.24; found C 55.71, H 7.80, N 36.11.

X-ray Structural Analysis: Table 1 contains the crystallographic data and details of the refinement procedure for compound **4**. The reflections were collected with a Nonius−Kappa CCD-diffractometer (graphite-monochromated Mo-K_α radiation). The structure was solved by direct methods (SHELXS-97[24]). The structural parameters of the non-hydrogen atoms were refined anisotropically by a full-matrix, least-squares technique (F^2). All hydrogen atoms were refined isotropically. Refinement was carried out with SHELXL-97.[25]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-236465. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223-336-033, E-mail: deposit@chemcrys.cam.ac.uk].

Acknowledgments

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