Two-Photon Absorption

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Boron-Containing Two-Photon-Absorbing Chromophores: Electronic Interaction through the Cyclodiborazane Core**

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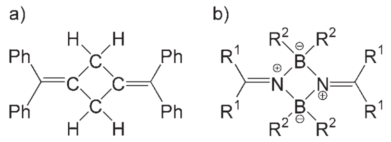
Conception of novel chromophores exhibiting two-photon absorption (TPA) is of growing importance nowadays due to the great variety of applications of this nonlinear optical (NLO) property,[1] which include two-photon excited fluorescence (TPEF) microscopy of biological systems,[2] three-dimensional microfabrication,[3] optical limiting,[4] data storage, and photodynamic therapy.[5] Since the prediction of this phenomenon by Göppert-Mayer in 1931,[6] many theoretical studies have been made on mono- and multidimensional chromophores.[7] Experimentally, symmetrical one-dimensional chromophores typically consist of two donor or acceptor groups that interact through a conjugated system. For example, the donor–acceptor–donor and acceptor–donor–acceptor chromophores described by Marder et al. can be regarded as π-conjugated molecules that undergo large changes in quadrupole moment on excitation.[8] Another approach was proposed by Andraud, Baldeck et al., who pointed out that TPA cross sections of oligomers are enhanced by biexcitonic coupling between two weakly conjugated monomers.[9] This theoretical approach led to the molecular engineering of several new efficient TPA chromophores and, in our hands, to water-soluble TPEF chromophores for bioimaging.[10]

In most cases the electronic interaction proceeds via conjugated systems. Recently, some computational studies have shown that the traditional π-conjugated transmitter in hyperpolarizable donor–acceptor systems could be replaced by a system of σ bonds to give π–σ–π through-bond coupling.[11] Furthermore, experimental data on 1,3-bis(diphenylmethylene)cyclobutane (Scheme 1a) have shown that in such a structure the two π systems interact electronically through the 1,3-dimethylenecyclobutane core.[12] Cyclodiborazanes (Scheme 1b), widely studied by Chujo et al., mainly for the preparation of conjugated polymers, are heteroatomic analogues of 1,3-dimethylenecyclobutane derivatives.[13] Many of the cyclodiborazane-based polymers are fluorescent and electroluminescent. They were also expected to show interesting third-order NLO properties.[13b] These experimental results suggested that the cyclodiborazane core maintains some kind of conjugation (1,3-π-type interaction) between the π systems across its square structure.



Scheme 1. 1,3-Bis(diphenylmethylene)cyclobutane (a) and cyclodiborazanes (b).

We report here the synthesis and characterization of a new TPA chromophore containing a cyclodiborazane central core. Our aim was to check the influence of this unusual structure on the efficiency of TPA properties due to electronic coupling through such a pseudoconjugated system. Our target chromophore **1** is shown in Figure 1.

Bis(4-iodophenyl)cyclodiborazane core **4** was obtained in 60% yield by classical hydroboration dimerization of 4-iodobenzonitrile (**2**) with mesitylborane (**3**; Scheme 2).[13a] Product **4** was obtained as a mixture of two stereoisomers in a 1:1 ratio (^{1}H NMR spectrum in the Supporting Information). Considering the different substituents in the cyclodiborazane structure, **4** can exist as four stereoisomers (Scheme 3).[14] The mesityl groups can be *cis* or *trans* with respect to each other, and the Ar groups can be in *syn* or *anti* configurations. Thus, *cis-syn* (**A**), *cis-anti* (**B**), *trans-syn* (**C**),

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

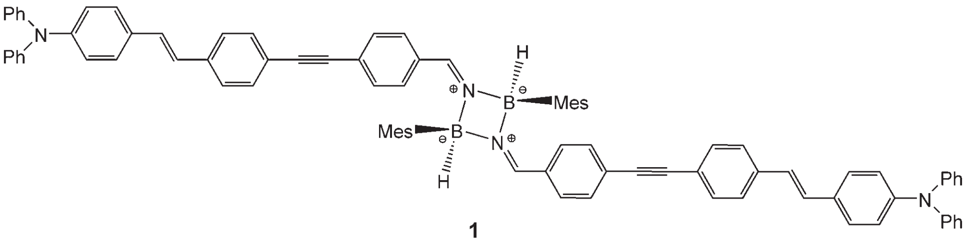
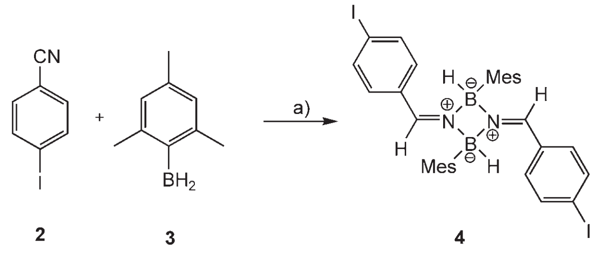
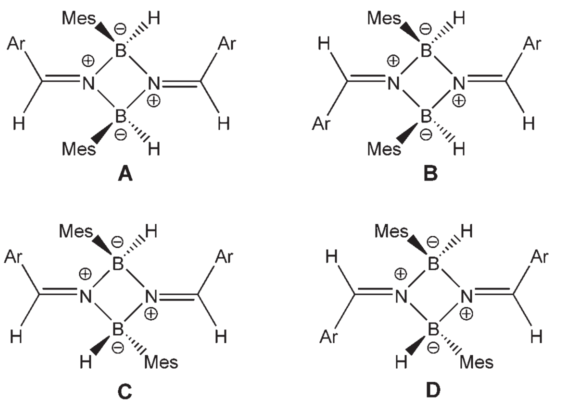


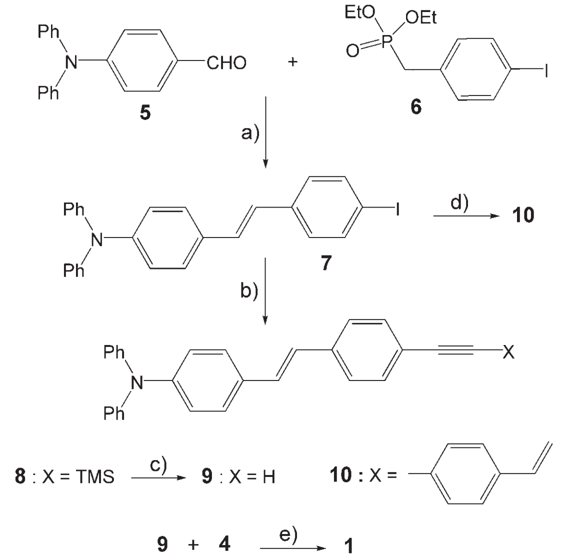
Figure 1. Structure of chromophore **1**.



Scheme 2. Synthesis of bis(4-iodophenyl)cyclodiborazane core **4**. a) THF, 0 °C, 15 min; 25 °C, 12 h; 60 %.



Scheme 3. Possible stereoisomers of tetrasubstituted cyclodiborazanes.



Scheme 4. Synthesis of chromophore **1** and model compound **10**. a) NaH, THF, 3 h, 55→66 °C, 85 %; b) $Me_3SiC{\equiv}CH$, $[PdCl_2(PPh_3)_2]$ 6 mol %, CuI 10 mol %, THF/iPr$_2$NH, RT, 48 h, 90 %; c) TBAF, THF, 15 min, RT, 80 %; d) 4-ethynylstyrene, $[PdCl_2(PPh_3)_2]$ 6 mol %, CuI 10 mol %, NEt$_3$, RT, 70 %; e) PdCl$_2$ 10 mol %, Cu(OAc)$_2$·H$_2$O 1.5 mol %, PPh$_3$ 40 mol %, THF, Et$_3$N, 80 °C, 12 h, 70 %.

and *trans-anti* (**D**) stereoisomers are possible. The *trans-syn* and *trans-anti* isomers (**C** and **D**) have been proposed as the most stable, but with no experimental evidence. We calculated the heats of formation for each stereoisomer by the AM1 method and found 269.0, 247.5, 238.7, and 232.0 kJ mol^{-1} for **A**, **B**, **C**, and **D** respectively.[15] These computational results clearly show that the *cis* arrangement of the mesityl groups in **A** and **B** is disfavored. Since we obtained only two stereoisomers for **4**, we can deduce that it consists of a mixture of **C** and **D**.

The synthesis of chromophore **1** is shown in Scheme 4. (*E*)-4-Iodo-4′-diphenylaminostilbene (**7**) was prepared by Wadsworth–Emmons condensation between commercially available 4-(diphenylamino)benzaldehyde (**5**) and diethyl 4-iodobenzylphosphonate (**6**) in the presence of sodium hydride. Trimethylsilylacetylene was subjected to Sonogashira coupling with **7** to give **8** in 85 % yield. The trimethylsilyl (TMS) group was removed by tetrabutylammonium fluoride (TBAF) in THF to yield ethynyl derivative **9**. Sonogashira coupling of **4** with 4-diphenylamino-4′-ethynylstilbene (**9**) led to a mixture of two stereoisomers, from which stereopure chromophore **1** was isolated in 55 % yield after column chromatography. It was fully characterized by ^{1}H, ^{11}B, and ^{13}C NMR and IR spectroscopy and HRMS. In the ^{1}H NMR spectrum, the imino resonance is located at δ = 8.1 ppm, as already reported for other cyclodiborazane structures.[16] The protons linked to boron give a very broad signal around 5.3 ppm. The ^{11}B NMR signal appears at δ = 5.6 ppm. Complete NMR characteristics are given in the Supporting Information. In the IR spectrum, the C=N band at 1641 cm^{-1} and B–H band at 2390 cm^{-1} are in agreement with previous reports.[14a] The stereochemistry of **1** was definitively proved by X-ray crystallography. X-ray-quality crystals were grown by slow diffusion of pentane into a concentrated chloroform solution. It was identified as the *trans-anti* **D**-type isomer. This confirms the stereochemistry of the most stable isomer predicted by our computational studies and the earlier predictions by Hawthorne.[14a] An ORTEP plot of **1** is presented in Figure 2. Color figures are available in the Supporting Information.[17]

This is, to our knowledge, the first structure showing the actual stereochemistry of a tetrasubstituted cyclodiborazane. The central square ring is totally planar (torsion angle B1-N1-

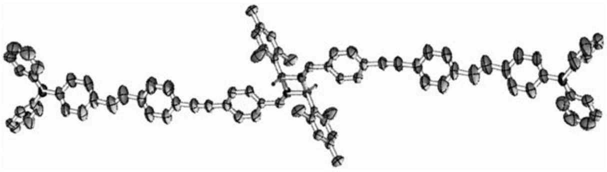


Figure 2. ORTEP plot of chromophore **1** showing the **D**-type stereochemistry.

B2-N2 0.0°). The phenyl rings attached to the cyclodiborazane moiety slightly deviate from planarity (torsion angle B1-N1-C1-C2 7.2°). The N–N distance of 2.17 Å is short enough to permit electronic coupling between the two conjugated systems. This N–N distance is similar to those reported for symmetric cyclodiborazanes and is close to the C_{sp^2}–C_{sp^2} distance of 2.12 Å reported for 1,3-dialkylidene cyclobutanes.[18]

Given that the starting diiodo compound **4** is most probably a mixture of **C** and **D** structures, we can assume that the other stereoisomer of **1** has **C** stereochemistry. It has been isolated and its study is in progress.

The optical properties of **1** were investigated in CH_2Cl_2 by UV/Vis absorption and fluorescence emission spectroscopy (all spectra in the Supporting Information). For comparison we also prepared the styrene "monomer" **10**, that is, a conjugated system linked to the nitrogen atoms of the cyclodiborazane core by a double bond. Compound **10** was obtained from **7** by Sonogashira coupling with 4-ethynylstyrene (Scheme 4). The absorption maxima are located at 403 nm ($\varepsilon = 1.0 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$) and 392 nm ($\varepsilon = 4.3 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$) for **1** and **10**, respectively. Thus, chromophore **1** exhibits a slight bathochromic shift of 11 nm in comparison with the model "monomer" **10**. Both chromophores are luminescent: $\lambda_{max} = 557$ nm for **1** and $\lambda_{max} = 491$ nm for **10**. A marked bathochromic shift of the emission band is observed for **1** in comparison with **10**. These results show a large difference ($\Delta = 1718\,\text{cm}^{-1}$) in the Stokes shifts of **1** and **10**. This indicates that the two conjugated systems linked to the cyclodiborazane core are strongly coupled in the excited state, but weakly coupled in the ground state. Such behavior has already been reported for the coupling of phenylacetylene chromophores in *meta* conjugation around a phenyl ring.[19] This led us to consider the photophysical properties of chromophore **1** in the light of the exciton model. The use of the exciton model to understand the photophysics of covalently bonded conjugated molecules is not new.[20]

According to the theory, purely excitonic coupling should lead to large shifts in both absorption and emission spectra. Since we observed a large shift only for the emission, it appears that a through-bond electronic interaction likely occurs essentially in the excited state.[19] This interaction was evidenced by molecular modeling. Selected AM1 calculated molecular orbitals of **1** are depicted in Figure 3. The HOMO−1 and HOMO are quasidegenerate in energy, and this is also the case for the LUMO and LUMO + 1. These two pairs of orbitals differ essentially in symmetry properties. We can observe from the HOMOs that in the fundamental state the electronic density is located around the terminal diphenylamino moieties, while the LUMOs show clearly that an electronic delocalization actually occurs along the whole conjugation pathway of the molecule. In the LUMO + 1 (Figure 3 a) orbital overlap is present across the cyclodiborazane ring and thus allows conjugation between the two donor groups in the excited state.

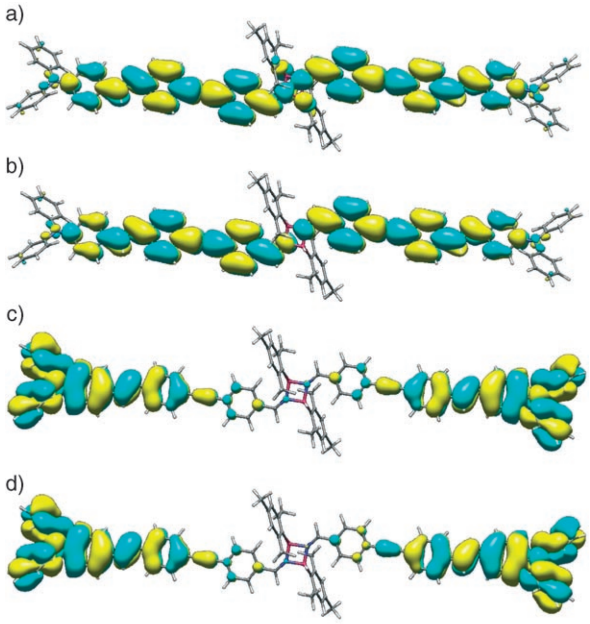


Figure 3. AM1 calculated molecular orbitals of chromophore **1**: a) LUMO + 1 ($E = -0.9984$ eV); b) LUMO ($E = -1.0054$ eV); c) HOMO ($E = -7.8874$ eV); d) HOMO−1 ($E = -7.8885$ eV).

Two-photon absorption properties are directly related to the third-order nonlinearity γ. Thus, we calculated the hyperpolarizability γ of chromophore **1** using the finite-field method, which has been already used to calculate the hyperpolarizabilities of boron-containing NLO chromophores.[21] We found $\gamma_0 \approx 1730 \times 10^{-36}$ esu. This high γ value is in agreement with the TPA cross section σ_2 of **1** that was experimentally determined in dichloromethane by the way of its two-photon induced fluorescence emission.[22] Indeed, **1** exhibits a strong two-photon absorption band in the near-IR region, centered at 830 nm with $\sigma_2 = 1350$ GM (1 GM = $10^{-50}\,\text{cm}^4\,\text{s}\,\text{photon}^{-1}$). The TPA spectrum is shown in Figure 4.

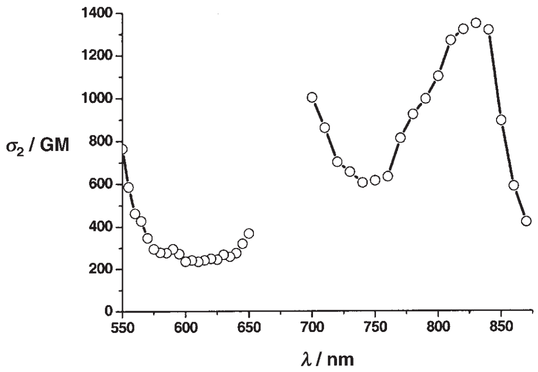


Figure 4. Two-photon absorption cross section of **1** in CH_2Cl_2.

A TPA chromophore having the same carbon skeleton as **1**, but without the cyclodiborazane central core and with $NOct_2$ donor groups in place of NPh_2, has $\sigma_2 = 950$ GM at 800 nm.[23] Given that NR_2 instead of NAr_2 does not affect significantly the TPA cross section,[8b] we conclude that the electronic effect induced by the cyclodiborazane core significantly increases the TPA cross section in comparison with two conjugated systems linked only by a σ bond.

In conclusion, we have prepared a new type of efficient centrosymmetric one-dimensional TPA chromophore based on the interaction between two donor groups through the incompletely conjugated cyclodiborazane core (π–σ–π through-bond coupling). This strategy afforded a fluorophore with a TPA maximum in the range of laser wavelengths used in two-photon microscopy. This opens the way to the use of new boron-containing TPA chromophores in biological sciences. The *trans-anti* stereochemistry around the central core was proved by X-ray crystallography. The study of the other stereoisomer of chromophore **1** that is in progress will provide information on geometrical effects on the electronic coupling and its influence on the TPA properties.

Experimental Section

Syntheses: Full synthetic experimental details and analytical data can be found in the Supporting Information.

X-ray crystal structure of chromophore **1**: Details on data collection, structure solution, and additional ORTEP plots are given in the Supporting Information.

Computational studies: Geometry optimization of the chromophore was performed with the MOPAC program within the InsightII and Cerius^2 interfaces from Accelrys (http://www.accelrys.com) with the AM1 Hamiltonian. Static hyperpolarizabilities were calculated by the finite-field method incorporated in the MOPAC program.

The TPA cross-section spectra were obtained by up-conversion fluorescence measurements (details in the Supporting Information).[22]

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[17] CCDC-609596 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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