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Synthesis and spectral characterization of bisnaphthylmethyl and trinaphthylmethyl cations

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Abstract—Cationic triarylmethane dyes containing one, two or three naphthalene moieties have been prepared. Their synthesis and preliminary spectral, nonlinear optical and theoretical characterization are reported here. The major electronic and steric hindrance effects of the 1,4-linked naphthalene have been examined by comparison of the UV–vis absorption of the 1,4-linked and 2,6-linked series.

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1. Introduction

Triarylmethane cations (TAMCs) such as crystal violet have been the subject of numerous investigations of their physical and photophysical chemistry.[1,2] The applications for these dyes range from biochemistry[3] to optical data storage.[4] We are interested here in their properties as nonlinear optical (NLO) chromophores and especially their multipolar properties.[5] In order to increase the first hyperpolarizability of crystal violet, researchers have modified TAMC structures by incorporation of different heterocycles[6] as well as stilbene[7] and phenylethynyl groups.[8] At the same time, there have been attempts to shift the main absorption band to the near infrared. TAMCs with multiple naphthyl groups have been described but often not isolated and fully characterized.[9–11] An objective of this study has been the synthesis of some bisnaphthyl and trinaphthylmethane cations and the comparison of their UV–vis spectra with those of some well-known TAMCs.

2. Synthesis

TAMC synthesis can be accomplished by two main methods. The first route involves the reaction between a bis-dialkylaminoketone and an arene or heterocycle in the presence of $POCl_3$.[12] The second synthetic pathway involves the use of the bis-dialkylaminoketone and an organolithium reagent to form the corresponding carbinol, followed by ionization after treatment with an inorganic acid such as perchloric acid. The experience of most investigators indicates that the latter route is more useful and can be extended to the synthesis of many TAMCs.[13] In any case, for either route, we must prepare the requisite naphthyl derivatives related to Michler's ketone, bis(6-pyrrolidinonaphtalen-2-yl) methanone (**1**) and bis(4-pyrrolidinonaphtalen-1-yl) methanone (**2**) in Scheme 1.

The synthesis of such diarylketones has been described and usually requires a multistep synthesis.[14] We have successfully employed a one step method developed by Olah and co-workers[15] based on the reaction between an aryllithium reagent and *N*-carboethoxypiperidine. The synthesis of ketone **1** starts from 6-bromo-2-naphthol which is transformed into 6-bromo-2-naphthalamine by Bucherer reaction, alkylation with 1,4-diodobutane to provide 6-bromo-2-pyrrolidinonaphthalene and, finally, conversion to an organolithium reagent and reaction with *N*-carboethoxypiperidine to form the ketone **1** in good yield (56%) and useful overall yield (22%).

The preparation of ketone **2** proved to be more problematic. The first challenge was the preparation of

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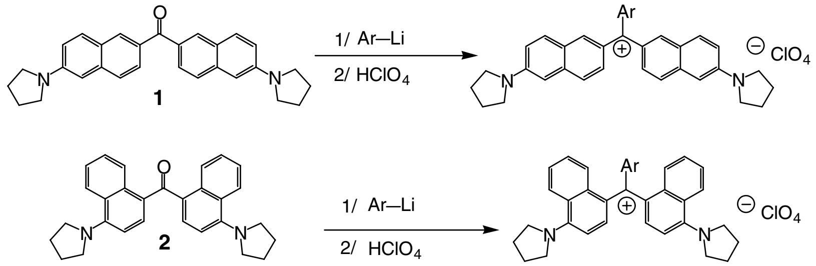


Scheme 1. Synthetic pathway for the preparation of bisnaphthylmethyl and trinaphthylmethyl cations.

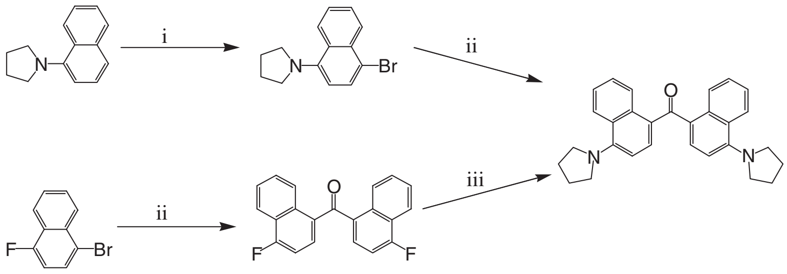
4-bromo-1-naphthalamine. Direct reaction of 1-naphthylamine with elemental bromine resulted in a complex mixture of mono-, di- and polybromination products.[16] Amongst the bromination reagents examined, 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one proved to be the most effective to produce the desired 4-bromopyrrolidinonaphthalene.[17] In contrast to the case of ketone **1**, the organolithium derivative of 4-bromopyrrolidinonaphthalene afforded ketone **2** in poor yield (<10%). This difference in reactivity between the 1,4- and 2,6-naphthyl isomers can be explained by the greater peri steric demands in the 1,4-isomer. To circumvent this problem we modified our strategy and used instead 1-bromo-4-fluoronaphthalene to give bis(4-fluoronaphtalen-1-yl) methanone. The pyrrolidine donors were next introduced by aromatic nucleophilic substitution. The two approaches examined for preparation of ketone **2** are described in Scheme 2.

The preparation of the bisnaphthyl and trinaphthylmethyl cations has been performed by reaction between the ketones **1** and **2** with an organolithium reagent and then treatment of the reaction mixture with perchloric acid (Scheme 1). We have used organolithium reagents obtained by bromine–metal exchange from 4-bromopyrrolidinobenzene, 4-bromopyrrolidinonaphthalene, 6-bromo-2-pyrrolidinonaphthalene, or by acid/base reaction from phenylacetylene and 1-(4-ethynylphenyl)-pyrrolidine. It is important to note that even if the carbinol can be prepared, in some cases the isolation of the cationic salt is not possible, as in the cases when Ar is either a phenyl, an ethynylphenyl or a 1-(4-ethynylphenyl)-pyrrolidine. In successful cases the carbocation was isolated in a yield between 42% and 80%.

3. Spectral characterization

It is known that the modification of a donor group in a charge transfer chromophore can have a large influence on the UV–vis spectrum. Thus, within a series of triarylmethyl cations, the substitution of the dimethylamino group by most dialkylamino or cycloaliphatic amine groups causes a red shift of the main absorption band due to the increased electron donation.[18]

The substitution of 4-pyrrolidinophen-1-yl by 4-pyrrolidinonaphthalen-1-yl also produces a bathochromic shift as charge transfer through the naphthalene is more facile than in benzene due to the difference in resonance energy. At the same time, the annulated ring in the 1,4-substituted naphthalene will be a steric obstacle to planarity of the cation contributing to a hypsochromic effect. These two effects are in opposition. Comparison of the UV–vis spectra (Fig. 1) of the molecules with one, two and three 1,4-linked (transverse) naphthalene moieties (**bPN14**, **bN14P** and **tN14**, respectively) indicates that the electronic contribution is dominant, as increased bathochromic shifts are observed with each 1,4-naphthalene addition (Table 1). To better understand this behaviour, we performed a series of ab initio geometry optimizations and molecular orbital calculations (RHF and MCSCF) with GAMESS.[19] The geometry of the molecules was optimized using RHF theory with an effective core potential and the Stevens/Basch/Krauss/Jasien/Cundari (SBKJC) basis. For **bPN14** (2 phenyls, 1 transverse naphthalene) and **bN14P** (1 phenyl, 2 transverse naphthalenes) we find that the unsubstituted phenyl(s) become more planar (a 29° twist for phenyls in **bPN14** and a 26° twist for the phenyl in **bN14P**, as compared to ca. 33° for the phenyls in **tP**),



Scheme 2. Two synthetic strategies for the preparation of bis(4-pyrrolidinonaphtalen-1-yl)methanone. Reagents and conditions (i) 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one, CH_2Cl_2, −10 °C; (ii) *n*-BuLi, THF, −78 °C, *N*-carboethoxypiperidine; (iii) pyrrolidine, DMSO, reflux.

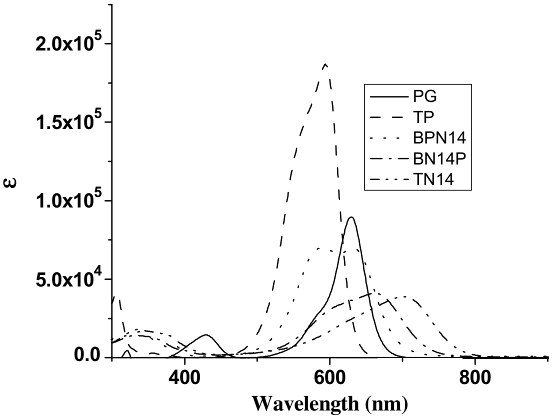


Figure 1. Molar extinction coefficients of the transverse naphthyl series in ethanol solution (ca. 10^{-5} M, ε is in $1 \times \text{mol}^{-1}\ \text{cm}^{-1}$ and λ in nm).

whereas the 1,4-naphthyl substituents are rotated 45°–50°. MCSCF calculations show that the first excited states of these molecules are well approximated by the transfer of one electron from the HOMO to the LUMO of the RHF ground state. The HOMO in each of these molecules is on the naphthyl substituents, while the LUMO is mainly concentrated on the central carbon and also spreads to the phenyl(s) (Fig. 2). Thus, raising the energy of the HOMO through 1,4-naphthyl substitution is offset by the decreased conjugation, but the increased conjugation of the phenyl(s) lowers the LUMO slightly, leading to overall moderate red shifts.

The substitution of a pyrrolidine group (in **tP**) by a hydrogen (in pyrrolidine green, **PG**) results in a red shift of about 36 nm. Akiyama et al.[20] explain this by the observation that all highly symmetrical molecules have a degeneracy of their HOMO and the substitution of one pyrrolidine group by one hydrogen breaks this degeneracy and decreases the transition energy. More specifically, calculations show that while the H-substituted ring in PG has a torsion angle of ca. 45°, the unsubstituted phenyls become more conjugated (torsion angle of 29°). MCSCF calculations show that the HOMO is spread over the unsubstituted phenyls and the LUMO has moderate representation there as well. It results in increased conjugation of these phenyls decreases amount of energy needed to transfer an electron to the LUMO.

The variations in the absorption bands of the TAMCs can also be explained by the calculations. The UV–vis spectra of the TAMCs are composed mainly of two bands (x and y) whose calculations shown are HOMO to LUMO and HOMO-1 to LUMO transitions, respectively. In **PG**, the large twist angle of the H-substituted phenyl leads to the large bathochromic shift of the y-band. This separation of x- and y-bands is not seen in bN14P (and possibly bPN14 and others as well), where the phenyl along the *y*-axis is much more conjugated form. This is supported by MCSCF calculations which suggest that x and y bands of bN14P are only separated by 18 nm.

Just as the enhancement of the donor group may induce a bathochromic shift, the extension of the conjugated pathway may act in the same direction. The substitution of a phenyl by a 2,6-linked naphthalene (longitudinal naphthalene) moiety extends the conjugated bridge, but does not introduce the steric effect characteristic of the transverse naphthalene. Calculations show that the twist of the longitudinal naphthalenes in all of the compounds studied does not deviate much (±5°) from 33° twist of the phenyls in **tP**. Nevertheless, the electronic effect in this kind of 2,6-linkage is smaller than seen previously. There are red shifts with the addition of longitudinal naphthalene moieties, ca. 100 nm between **tP** (3 phenyls) and **bPN26** (two phenyls, one longitudinal naphthalene) and ca. 200 nm between **tP** and **tN26** (three longitudinal naphthalenes). In contrast to the transverse naphthalene substitutions, where each additional substitution produces a greater red shift, this is not the case for the longitudinal systems, as compound **bN26P** possesses a band at shorter wavelength than **bPN26**. The reason for this is not completely understood. In general, the smaller steric effect in the 2,6-naphthyls suggests that the degeneracy of the HOMO and HOMO-1 is less important in this system. We believe the results for the 2,6-naphthyls are a consequence of the LUMO in these molecules being less concentrated on the central carbon and more spread out onto the napthyl rings. This conjugation, of course, lowers the energy of the LUMO and hence the excitation energy of the molecules. Thus the red-shifts in the 2,6-naphthyls are primarily related to a decrease in the energy of the LUMO.

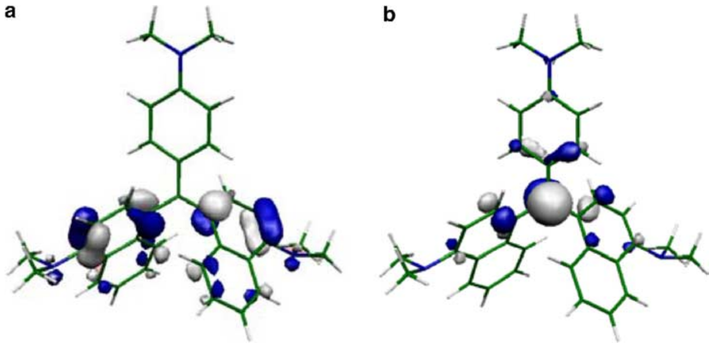
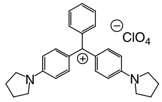
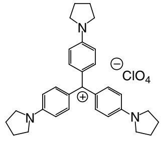
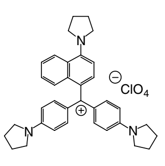
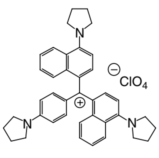
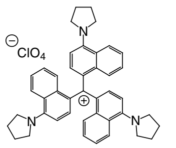
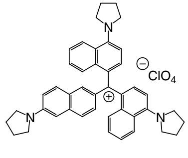
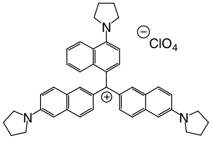
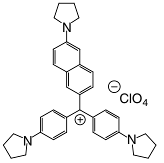
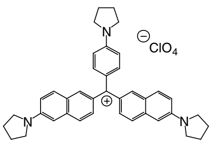
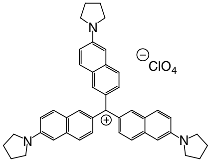


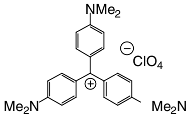
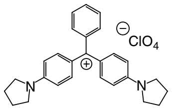
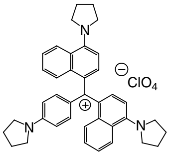
Figure 2. Singly occupied orbitals in the first excited state of BN14P (a) lower lying (RHF HOMO) SOMO, (b) higher lying (RHF LUMO) SOMO. Note the large charge transfer in the *y* (symmetry axis) direction, which produces a large NLO response. Graphics were made using Molekel[22] software.

Table 1. Spectroscopic properties of TMAC chromophores in ethanol solution (ca. 1×10^{-5} M)

Compound	 **PG**	 **tP**	 **bPN14**	 **bN14P**	 **tN14**
$\lambda_{\max}$ (ε)	630 (8.96 10^4)	594 (1.87 10^5)	587 (6.98 10^4) 633 (6.96 10^4)	662 (4.10 10^4)	701 (3.88 10^4)
$\Delta\lambda$	49	77	119	131	137
Compound	 **bN14N26**	 **bN26N14**	 **bPN26**	 **bN26P**	 **tN26**
$\lambda_{\max}$ (ε)	702 (5.21 10^4)	701 (2.9 10^4)	697 (8.47 10^4)	668 (6.81 10^4)	790 (9.83 10^4)
$\Delta\lambda$	148	162	148	124	141

$\lambda_{\max}$ is given in nm, ε in $1 \times \mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$, and $\Delta\lambda$ represents the full width in nm at half maximum.

Table 2. Absolute value of the rotational invariants of the hyperpolarizability (10^{-30} esu) obtained from TCSPC-45°-HRS

	 Crystal Violet	 Pyrrolidine Green	 bN14P
$\|\|\beta_{1ss}\|\|$	393 ± 30	226 ± 19	655 ± 35
$\|\|\beta_{3ss}\|\|$	240 ± 19	229 ± 27	361 ± 20
$\|\|\beta_{1mm}\|\|$	255 ± 21	337 ± 32	429 ± 26
$\|\|\beta_{2mm}\|\|$	200 ± 17	275 ± 27	360 ± 23

A common effect of the extension of the aromatic core in the naphthalene derivatives is a broader absorption band than in the triphenylmethyl cation series that typically have a width (at half height) between 50 and 80 nm. On the other hand, in the TAMCs where at least one naphthalene moiety is incorporated, this value increases to a range between 119 and 141 nm. This expansion of the bandwidth results in absorption tailing into the near infrared, especially in the case for **tN26** (Table 1).

To understand the influence of these structural modifications on the NLO properties, we have undertaken a series of measurements of the first hyperpolarizability of these new TAMCs by the time-correlated single photon counting 45° hyper-Rayleigh scattering (TCSPC-45°-HRS) technique. The TCSPC method distinguishes HRS from two-photon fluorescence in the time-domain, resulting in improvement of the accuracy of measurements of Kleinman-disallowed components. This measurement permits the figure of merit of this kind of compound for chiral axial nonlinear optical media.[21] The measurements of these second order non-linear optical properties are more sensitive to the nature, symmetry and overlap between the various orbitals. The results obtained for the compound **bN14P** and two other classical TAMCs are summarized in Table 2. We see that **bN14P** possesses better nonlinear properties than crystal violet in both the dipolar and the Kleinman disallowed parts, due to a large charge transfer from the ground to first excited state. This indicates the potential of these new bisnaphthyl and trinaphthylmethyl cations for NLO applications.

Acknowledgement

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Supplementary data

Synthetic methods and spectroscopic data for the compounds discussed here are provided along with a brief description of the light scattering experiments. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.05.138.

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