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Synthesis, structure and nonlinear optical properties of some chiral chromophores derived from L-proline

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Abstract—A series of chiral donor-π-acceptor chromophores with potential for nonlinear optical activity has been synthesised utilising a donor derived from L-proline as the source of chirality. The compounds feature both organic and organometallic acceptor end groups and were assessed for second harmonic generation by the Kurtz powder technique and in one case by hyper-Raleigh scattering. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the early 1990s Yadav and co-workers reported briefly that **1** condenses with active methylene compounds to afford dicyano vinyl and vinyl dicarboxylates.[1] More recently Aitken has revisited this system and extended this reaction to include monoesters and ketones.[2] The products of these reactions are in essence highly polarised donor-π-acceptor (D-π-A) systems and it is well known that this motif is among the best arrangements for the design of second-order nonlinear optical (NLO) compounds.[3] Recently we have had a strong interest in achiral[4] and chiral[5] organic/organometallic hybrid NLO systems. It occurred to us that **1** represents a rigid framework for attachment of a nitrogen donor atom to the π-bridge and so may lead to more effective communication between donor and acceptor. Chirality is an important issue in the design of such chromophores since the measurement of bulk NLO properties in the solid state (necessary for device manufacture) is dependent on a noncentrosymmetric packing environment within the crystal lattice.[6] Several groups have reported the introduction of chirality into their chromophores using L-proline as a donor residue,[7] but to our knowledge no approaches have utilised the conformationally locked derivative of the molecule described here.

It is well established that increasing the length between acceptor and donor results in better second harmonic generation (SHG)[8] and so it was necessary to include a longer π-bridging element than the sole double bond introduced previously.[1,2] To do this we condensed **1** with the sodium enolates of **2** or **3** in order to provide us with phenyl- or thienyl-containing bridges linked via an unsaturation to the donor (Scheme 1). This yielded **4a** and **4b** in good to excellent yields and in which the nitrogen and the aryl groups occupied a *cis*-relationship about the alkene as shown by NOE experiments. Removal of the redundant ester by decarboxylation and concomitant isomerisation of the alkene afforded exclusively the desired *trans*-isomers **5a** and **5b** (Scheme 1), the configurations of which were also confirmed by NOE experiments. In a related approach **8** was prepared in which the bridging portion of the molecule was attached by an imine linker, a motif which has enjoyed considerable success in SHG previously (Scheme 1). 4-Bromoaniline condensed with **1** directly but it proved difficult to isolate the free base from the resulting iminium salt and so the lithium amide generated from 4-bromoaniline and butyllithium was used to form **7** in excellent yield. Aldehyde functionalities were desired for subsequent elaboration into stronger acceptor residues and these were easily introduced by metal halogen exchange (in **4a** and **7**) or lithiation (in **4b**) with butyllithium followed by DMF quench, affording **6a**, **6b** and **8** in good overall yields (Scheme 1).

Condensation of **6a**,**b** and **8** with malononitrile to complete the chromophores **9**, **10** and **11** proceeded under

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Keywords: iminium salts; nonlinear optics; Kurtz powder; hyper-Raleigh scattering; crystal structure.

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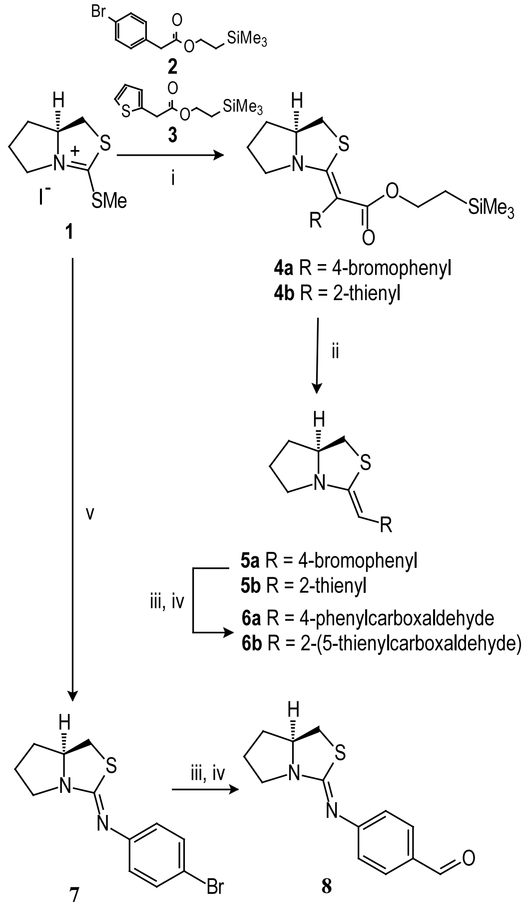
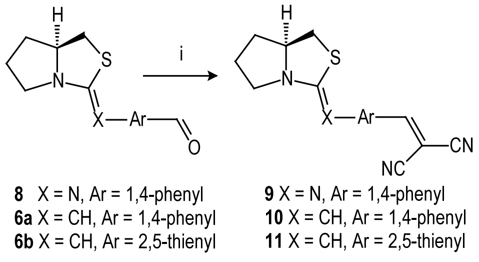


Scheme 1. *Reagents and conditions*: (i) THF, NaH, −78°C; (ii) TBAF, THF, reflux, 1 h; (iii) BuLi, THF, −78°C; (iv) DMF, H_2O; (v) 4-bromolithiumanilide, THF, −78°C.

mild conditions and in excellent yields (Scheme 2). Unfortunately it was not possible to record optical rotations for the highly coloured compounds **10** and **11**, even at low concentrations, since their broad absorption bands overlapped with the measurement frequency (546 nm). A single-crystal X-ray diffraction study of **9** (Fig. 1) was undertaken (see [†]).[9]



Scheme 2. *Reagents and conditions*: (i) malononitrile, triethylamine, THF, 1 h, rt.

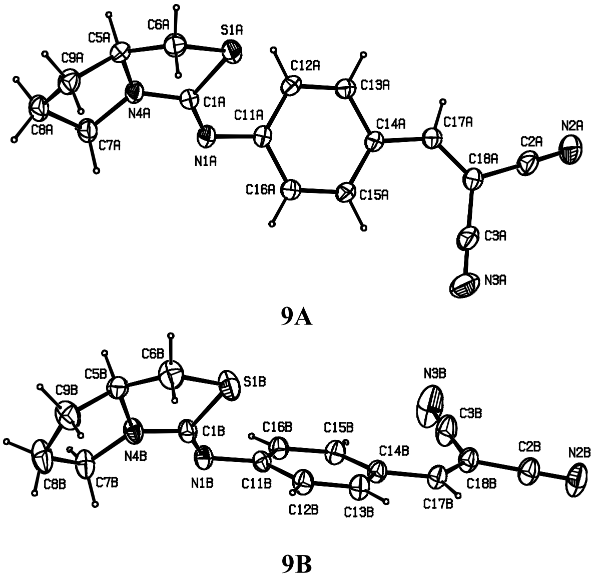
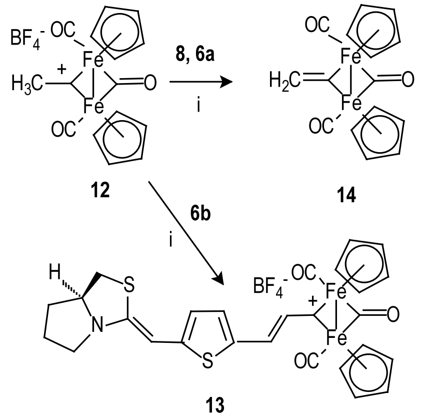


Figure 1. Molecular structures of the two molecules, **9A** and **9B**, in the asymmetric unit. Selected bond lengths: S1A–C1A 1.789(2), S1A–C6A 1.819(3), N1A–C1A 1.286(3), N1A–C11A 1.396(3), C1A–N4A 1.338(3), S1B–C1B 1.774(2), S1B–C6B 1.807(3), N1B–C1B 1.288(3), N1B–C11B 1.401(2), C1B–N4B 1.347(3) Å. Angles C1A–S1A–C6A 91.12(11), C1A–N1A–C11A 121.1(2), N1A–C1A–S1A 127.75(16), C1B–S1B–C6B 92.58(12), C1B–N1B–C11B 120.2(2), N1B–C1B–S1B 127.48(17)°.

The structure confirms the expected configuration about the imine double bond but it is evident from the normal bond lengths in the isothiourea subunit that there is not extensive delocalisation. It is noteworthy that there are pairs of molecules **9A** and **9B** in the asymmetric unit and the fused rings exhibit quite different torsion angles in the thiazole ring N4A–C1A–S1A–C6A 20.1(2)° in **9A** and N4B–C1B–S1B–C6B 6.5(2)° in **9B**.[†]

Previously we have synthesised a number of chromophores terminating in the powerful acceptor residue derived from **12**[4,5,8] utilising its well known condensation reaction with aldehydes to form carbyne complexes.[10] Most of the compounds have exhibited extremely high SHG in solution determined by hyper-Raleigh scattering (HRS).[11] Encouraged by this we attempted the condensation of **6a**,**b** and **8** with **12** (Scheme 3). The reaction usually proceeds to completion in refluxing dichloromethane within 18 h but in the case of **6a** and **8** after this period only **14**, the deprotonation product, was observed. Indeed, even after prolonged reaction times no other compounds were formed (determined by inspection of the IR spectrum of the reaction mixtures). However reaction with **6b** did afford the required complex **13** after 18 h, albeit in moderate yield. The basicity of the nitrogen donor atom is clearly important in this reaction and evidently a crossover point exists between **6a** and **6b**. As before, the melting point and optical rotation were impossible to obtain for **13**.

[†] Crystallographic data (excluding structure factors) for **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 178063. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].



Scheme 3. *Reagents and conditions*: (i) CH_2Cl_2, reflux 24 h.

It is informative to examine the UV spectra of potential NLO compounds since it has been established that a low-energy charge transfer band and solvatochromic behaviour may be indicative of good SHG.[12] For all the compounds there is an appreciable shift of the CT band to lower energies between the aldehyde precursors (themselves D-π-A compounds) and the completed chromophores (Table 1), indicating more delocalised structures in the latter. For **9**, **10** and **11** the λ_{max} band moves to lower energies caused by a change of imine (effectively the isothiourea subunit in **9** is not a very good donor as discussed earlier) to methine (**9** versus **10**) or benzene to thiophene (**10** versus **11** due to the lower resonance energy of the latter over the former) in the bridge. All the bands exhibit a small degree of solvatochromic behaviour (up to 0.5 kJ/mol between dichloromethane and acetonitrile solutions of **9**) (Table 1). When the dicyano vinyl acceptor is replaced with the much more powerfully accepting $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{-})]^+\ BF_4^-$ residue and the chromophore is in the optimal bridging configuration, then in **13** the λ_{max} band is found at much lower energies and is more solvent dependent (3.3 kJ/mol, dichloromethane/acetonitrile) (Table 1).

These findings suggested that some of these compounds may exhibit significant SHG and this was initially assessed by the Kurtz powder method which determines the bulk SHG response.[13] All the compounds were found to exhibit a powder response 0.00 times the urea standard. The dark colour of compound **13** prevented the visual detection of any decomposition caused by significant absorption at the second harmonic frequency and might also contribute to the poor results observed for this compound. It is important to stress that results obtained with the Kurtz powder method are very difficult to interpret in terms of molecular structure–property relationships, since they depend not only on the crystal packing but also on grain size and phase matching properties. Indeed many attempts to produce chiral NLO chromophores reported in the literature have resulted in zero or negligible powder responses.[14] This is often explained in terms of the unfavourable alignment of otherwise highly nonlinear optical chromophores in the crystal lattice but frequently no molecular hyperpolarisability measurements are reported to support this.

Although zero bulk responses were obtained in our study it does not follow that the molecular hyperpolarisabilties of these compounds are intrinsically zero. Previously we have recorded some extremely high β-values for organometallic merocyanines which incorporate the powerfully accepting $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{-})]^+\ BF_4^-$ residue.[4] The HRS technique[11] was used to obtain the hyperpolarisability (β) of our most promising compound **13** at 1064 nm using the external reference method. No fluorescence was detected at 532 nm, the second harmonic frequency, and β was found to be 632×10^{-30} esu. Generally β-values for organometallic chromophores fall within $50–700\times10^{-30}$ esu[15] and **13** is at the upper limit of this range.

To conclude, we have further extended the scope of the reaction first described by Yadav and shown that the chiral iminium salt **1** may be successfully functionalised in order to form new classes of compounds bearing remote reactive sites for further elaboration. Although

Table 1.

Compound	Yield (%)	Mp (°C)	$[\alpha]_{546}^{Hg}$ (°)	λ_{max}/nm ($\varepsilon\times10^3$)	
				CH_2Cl_2	CH_3CN
4a	99	121–122	+358.0	Colourless	Colourless
4b	73	78–79	−334.0	Colourless	Colourless
5a	87	81–82	−98.0	Colourless	Colourless
5b	73	Oil	–	Colourless	Colourless
6a	94	109–111	−436.0	402	398
6b	73	156–158	−321.2	435	435
7	99	58–59	+54.5	275	272
8	88	92–94	+204.4	325	321
9	86	128–129	+302.8	404 (29.0)	395 (27.0)
10	77	120 (Decomp.)	–	512 (10.4)	504 (10.2)
11	90	120 (Decomp.)	–	553 (58.8)	555 (52.8)
13	36	>300	–	665 (25.2)	653 (23.0)

no bulk powder NLO responses were recorded for these compounds, **13** was found to exhibit a very high molecular hyperpolarisability ($\beta = 632\times10^{-30}$ esu). We are currently investigating ways to capitalise on such high β-values by designing new generations of complexes which will exhibit large bulk SHG based around the organometallic acceptor group $[(C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C\text{-})]^+ BF_4^-$.

Acknowledgements

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