

Non-linear Optical Properties of Squarate Esters and Amides†

Michael G. Hutchings,^{*a} Ian Ferguson,^b Simon Allen,^c Joseph Zyss^d
and Isabelle Ledoux^d

^aBASF plc, PO Box 4, Earl Road, Cheadle Hulme, Cheshire SK8 6QG, UK

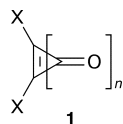
^bZeneca Specialties Research Centre, Blackley, Manchester M9 8ZS, UK

^cICI plc, Wilton Research Centre, P.O. Box 90, Middlesbrough TS90 8JE, UK

^dFrance Télécom, CNET, Centre Paris B, Laboratoire de Bagneux, 196 Avenue Henri Ravera, F-92220 Bagneux, France

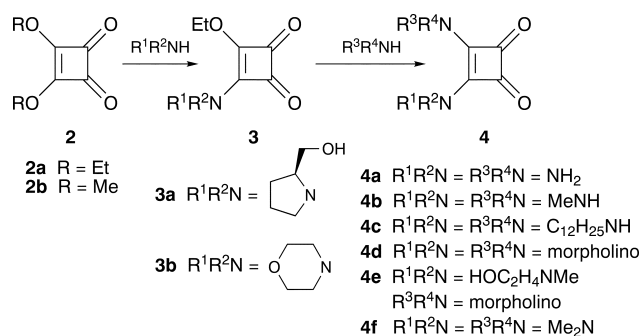
In agreement with theoretical prediction, a squaric acid diamide shows appreciable quadratic non-linear optical (NLO) activity in solution, and because of their transparency such amides may be attractive materials for second harmonic generation of blue light, although all crystalline derivatives measured were essentially NLO inactive.

A major potential use of organic non-linear optical (NLO) materials is frequency doubling, or second harmonic generation (SHG), of laser-generated light.^{1,2a} Near-infrared radiation of wavelength 830 nm from a semiconductor laser can in principle be converted into blue light of wavelength 415 nm by a suitable NLO material. One particular application of a device based on such a material is in optical data storage, where four times as much information could be stored per unit area of optical disc by writing the information with the SH radiation, compared with the fundamental wavelength. While this application of NLO materials has been much discussed, there are few materials which combine the desirable high NLO activity to bring about SHG with the transparency essential to allow passage of the shorter wavelength SH radiation. In fact, these properties are to a certain extent mutually incompatible, leading to the so-called transparency–non-linearity trade-off.^{2b} Consequently a major goal in the research of new organic NLO materials has been the design, synthesis, and optical characterisation of speculative materials having properties consistent with these fundamental requirements.



Recent theoretical studies³ on oxocarbon derivatives of generic structure **1** have been reported. Squarate (**1**; $n = 2$), croconate (**1**; $n = 3$), and rhodizonate (**1**; $n = 4$) esters and amides (**1**; $X = OR$ or NRR') were predicted to have relatively high NLO activity, especially considering their small molecular volumes, combined with transparency in the important blue region of the visible spectrum. In this paper, we report on experimental follow-up studies of the theoretical work, centred on the most easily accessible members of this series, a squarate diester **2a**, mixed amide esters **3**, and diamides **4** (Scheme). These molecules can be considered typical conjugated donor–acceptor systems, where alkoxy and/or amino donor groups are connected to the dicarbonyl acceptor unit by the unsaturated cyclobutene skeleton.

NLO results have been published on cyclobutenediones substituted by either a hydroxy or amino substituent in combination with a 4-*N,N*-dimethylaminophenyl group attached directly to the ring nucleus.⁴ However, these have absorbances bathochromic relative to the molecules reported



Scheme

in this study, and are unsuitable for SHG from a fundamental wavelength near 830 nm.

The commercially available diethyl diester of squaric acid (**2a**) was used as starting material for the preparation of the amides (Scheme). Reaction between the diester **2a** and one equivalent of amine led to the monoester monoamides **3**, and with further amine to the diamide **4**. Characterisation of products was unexceptional. The main problem encountered was the relative insolubility of some of the derivatives thus prepared, inhibiting recrystallisation as well as meaningful solution measurements. However, by inclusion of either relatively polar or long-chain hydrophobic substituents in the amines, several derivatives of sufficient solubility were ultimately prepared. The ester amide **3a** was intentionally based on homochiral prolinol as amine, ensuring that the homochiral product must crystallise in a non-centrosymmetric space group. Such a packing arrangement is a necessary (although not sufficient) condition for NLO activity in the crystal. Furthermore, the pendant hydroxy functionality could act as a source of attachment to a polymer backbone.

One of the attractive features predicted for squarate derivatives by MO calculations³ is their relative transparency. This is particularly significant for blue SHG. There is reasonable agreement between theoretical (gas phase) values calculated by the CNDOVSB method⁵ and experiment (Table 1); the absorption maxima of the squarate derivatives are indeed well into the UV. However, for practical purposes, the concentration of active chromophore in any NLO device will be much higher than that of the dilute solutions used for spectral measurements, so spectra of saturated solutions were also measured in order to determine the transparency cut-off wavelengths. The values found are far more bathochromic than might be anticipated from the dilute solution spectra (Table 1). However, they are still below the SH wavelengths of interest (*ca.*

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 NLO and other solution properties of squarate derivatives

No.	UV/VIS spectra (nm)			Dipole moments (D) and hyperpolarisability ($\times 10^{-30}$ esu)				
	Experimental ^a		Calc. ^b λ_{calc}	Calculated ^b			Experimental	
	λ_{max}	$\lambda_{\text{cut-off}}$		μ_0	β_0	$\beta_{1.17}$	μ_0	β_0
Squarate diesters								
2b			302	2.92	6.68	10.7		
2a	338	400					5.3	1.6
Squarate monoester, monoamide								
3a	281	390	319	6.09	8.44	13.59	6.3	2.4
Squarate diamides								
4f			356	7.57	10.56	20.77		
4d	304	400					7.0	12.0

^aChloroform solution. ^bRef. 3.

410 nm), and so the squarate esters and amides are potential materials for SHG of blue light.

The experimental hyperpolarisability values, β_0 , at zero field strength are determined by the EFISH technique at 1.06 μm ,⁶ β_0 being deduced from the experimental β value using a two-level dispersion model.⁶ These data are recorded for **2a**, **3a** and **4d** in Table 1, alongside experimentally determined ground-state dipole moments, μ_0 . For comparison, the theoretical results³ on comparable structures are also given in Table 1. The β_0 values for the diester and the ester amide are both low in comparison with calculated values. However, the value of 12×10^{-30} esu for the diamide **4d** is close to the value calculated for the comparable diamide **4f** ($\beta_0 = 11 \times 10^{-30}$, $\beta_{1.17} = 21 \times 10^{-30}$ esu). The magnitude of the hyperpolarisability is comparable with that measured for typical benzenoid donor-acceptor NLO materials such as 4-dimethylaminonitrobenzene [$\beta_0 = 10 \times 10^{-30}$, $\beta_{1.06} = 26 \times 10^{-30}$ esu; $\lambda_{\text{max}}(\text{EtOH}) = 388$ nm].⁷ The latter material is yellow and thus of no use for SHG of blue wavelengths. Furthermore, the hyperpolarisability per unit molecular volume is higher for the squaramide than for the nitro-aniline.

Crystalline materials **3a**, **3b** and **4a-4e** were colourless as expected. They were screened for SHG activity by the Kurtz-Perry powder method,⁸ but disappointingly most of the materials are NLO inactive ($< 10^{-3} \times$ urea standard). The two exceptions are the bis(dodecylamide) **4c** and the mixed esteramide **3b**. However, activity for each of these is only ca. 0.03 times that of the urea standard, and thus they are of no practical interest. The crystalline derivative **3a** containing the homochiral prolinol substituent is forced to pack in a non-centrosymmetric space group, but despite this it is NLO inactive implying the chromophore dipoles must still align more or less antiparallel in the crystal. A crystal structure determination of the squarate diamide **4d** revealed a centrosymmetric packing motif, with adjacent squarate chromophores oriented antiparallel with respect to one another.⁹

We conclude that squarate diamides have intrinsic quadratic NLO activity and transparency high enough for them to be technically useful materials for SHG. However, this is counterbalanced by our failure to find a suitable non-centrosymmetric crystalline form. Poled polymer films based on the diamides would be alternative synthetic targets.

Experimental

Synthetic routes followed a published procedure¹⁰ and gave products with satisfactory microanalytical and spectroscopic properties.¹¹ Molecular hyperpolarisabilities and dipole moments were determined by a published technique.^{6,12}

Received, 8th December 1997; Accepted, 7th January 1998
Paper E/7/08794B

References

- H. S. Nalwa and S. Miyata, in *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press, Boca Raton, FL, 1994.
- (a) J. Zyss (editor), *Molecular Nonlinear Optics, Materials, Physics and Devices*, Academic Press, Boston, 1994; (b) J. Zyss, I. Ledoux and J.-F. Nicoud, in ref. 2(a), p. 129.
- M. Dory, J.-M. André, J. Delhalle and J. O. Morley, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 2319.
- L. S. Pu, *ACS Symp. Ser.*, 1991, **455**, 331.
- V. J. Docherty, D. Pugh and J. O. Morley, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1179.
- J.-L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.
- M. Barzoukas, D. Josse, J. Zyss, P. F. Gordon and J. O. Morley, *Chem. Phys.*, 1989, **139**, 359.
- S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, 1968, **39**, 3798.
- J. Delhalle and M. Dory, personal communication.
- A. H. Schmidt, *Synthesis*, 1980, 961.
- Melting point/ $^{\circ}\text{C}$ (crystallisation solvent): **3a** 102–105 (toluene); **3b** 156–161 (ethanol) (lit.,¹⁰ 154–157; 156); **4a** 133 (water); **4b** 320–323 (ethanol); **4c** 173–174 (toluene) (lit.,¹⁰ 174–178); **4d** 275–277 (water) (lit.,¹⁰ 272–275); **4e** 129–133 (ethanol).
- M. G. Hutchings, I. Ferguson, D. J. McGeen, J. O. Morley, J. Zyss and I. Ledoux, *J. Chem. Soc., Perkin Trans. 2*, 1995, 171.