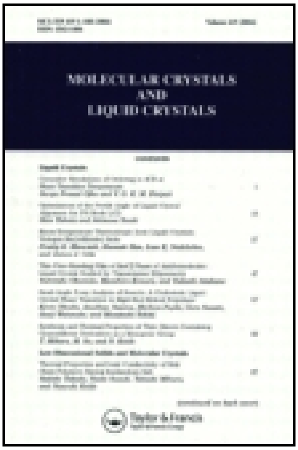


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Nonlinear Optical Properties of Diarylethenes

J. A. Delaire [a], I. Fanton-Maltey [a], J. Chauvin [a], K. Nakatani [a] & M. Irie [b]

[a] PPSM, UMR 8531 of CNRS, Ecole Normale Supérieure de Cachan, 61, avenue du Président Wilson, 94235, CACHAN Cedex, France

[b] Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6-10-1, Higashiku, Fukuoka, 812-8581, Japan

Version of record first published: 24 Sep 2006

To cite this article: J. A. Delaire, I. Fanton-Maltey, J. Chauvin, K. Nakatani & M. Irie (2000): Nonlinear Optical Properties of Diarylethenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 233-238

To link to this article: http://dx.doi.org/10.1080/10587250008023924

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 233-238
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Nonlinear Optical Properties of Diarylethenes

J.A. DELAIRE[a], I. FANTON-MALTEY[a], J. CHAUVIN[a],
K. NAKATANI[a] and M. IRIE[b]

[a]*PPSM, UMR 8531 of CNRS, Ecole Normale Supérieure de Cachan, 61, avenue du Président Wilson, 94235 CACHAN Cedex, France and* [b]*Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki 6–10–1, Higashiku, Fukuoka 812–8581, Japan*

Products $\mu\beta$ of the first order hyperpolarisabilities β of both isomers of dithienyl ethene derivatives by their ground state dipole moments μ have been determined experimentally by the EFISHG technique, then calculated by a semi-empirical method. Both calculations and measurements put into evidence a large increase in $\mu\beta$ in going from the open isomer (OF) to the largely π conjugated closed isomer (CF). This photoinduced change in second order NLO coefficient is used to modulate the Second Harmonic Generation (SHG) signal generated by a PMMA film doped with one diarylethene under alternate irradiation with UV (325 nm) and visible (514 nm) light.

Keywords: diarylethene; Second Harmonic Generation; photoswitching

INTRODUCTION

We have shown that a large change of first order hyperpolarisability coefficient (β) accompanies the photoinduced colour change of many photochromes.[1],[2] First put into evidence for the azo derivative Disperse Red One, this effect has also been demonstrated for spiropyran/photomerocyanine; in this last case, the β value is increased by a factor of 40 in going from the colourless spiropyran to the blue photomerocyanine. This increase is easily explained by an increase of the electronic delocalization of π electrons.

As already demonstrated by Lehn and coworkers [3], diarylethenes are especially well suited for this coupling between photochromic and NLO properties as light irradiation at well separated wavelengths can interconvert these molecules between two isomers in which the heterocycles are either conjugated or non conjugated.

In this contribution, we present both measurements and calculations of first order hyperpolarisabilities of both isomers of dithienylethene derivatives; then we describe an attempt to use this coupling between photochromism and second order NLO by measuring photoswitching of SHG signal in a PMMA film doped with one of these photochromes.

EXPERIMENTAL

The synthesis and the spectroscopic study of photochromism of the dithienylethenes studied in this work has already been described (see Table 1).

The experimental set-up for determination of μβ products by the Electric Field Induced Second Harmonic Generation (EFISHG) technique has already been described [4]. The fundamental beam is generated by a nanosecond Nd-YAG laser, whose fundamental radiation (1.064 μm) is Raman shifted towards a larger wavelength (1.907 μm) by passing through a high-pressure hydrogen cell. Second harmonic generation is detected at 953.5 nm by a photomultiplier tube (Hamamatsu R 5108) and the signal is averaged via a numerical oscilloscope (Tektronix.TDS 620B). Maker fringes are registered for pure solvent (dioxan) and solutions of increasing concentrations of the photochrome. μβ values are determined by comparison with a reference solute, methylnitroaniline (MNA), dissolved in the same solvent ($\mu\beta_{MNA}$= 71.06 10^{-48}esu).

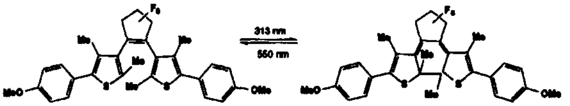
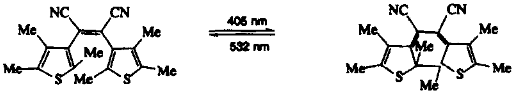
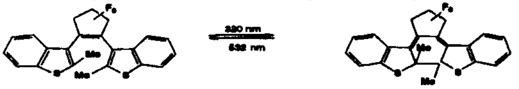
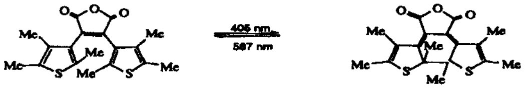
Dithienylethene derivatives	Ref.
1,2 bis (5-p-anisyl-2,4-dimethyl thiophène-3-yl) perfluorocyclopentene  OF1 CF1	[5]
1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl) ethene  OF2 CF2	[6]
1,2-bis(2-methylbenzo[b]3-thienyl) perfluorocyclopentene  OF3 CF3	[7]
2,3-bis(2,4,5-trimethyl-3-thienyl) maleic anhydrid  OF4 CF4	[6]

TABLE 1 : Dithienylethene derivatives studied in this work for their NLO properties.

PMMA films doped with dithienylethene derivatives were spin cast on a glass plate covered by ITO. The initial solution was prepared by dissolving 0.3 g of PMMA and 0.03 g of dithienylethene in 5 mL of chloroform. The films were dried at 100°C for 30 mn, then poled at 120°C under a Corona discharge (needle at 6 kVand grid at 800V, at 1 cm and 2 mm above the film surface respectively).

RESULTS AND DISCUSSION

Determination of hyperpolarisabilities of open (OF) and closed (CF) forms.

μβ values are given in Table 2. In order to determine μβ of closed forms, a solution of the open form in dioxan was irradiated during 10 hours under UV light (313 nm). A photostationary state was reached between the two isomers, and the composition of the solution was determined by measuring the absorbance of the visible band and the known absorption coefficients of the closed forms CF. As shown in Table 2, the conversion ratio is never 100 %, and this is a consequence of first, the choice of the irradiation wavelength (313 nm), and second, the existence of two conformers for OF, one "antiparallel" which gives the coloured form CF by a conrotatory cyclisation reaction, and the other "parallel", which cannot lead to cyclisation by a conrotatory process [8].

	[CF]/[OF] %	μβ (OF) 10^{-48} esu	μβ (CF) 10^{-48} esu
OF1/CF1	44	31	137
OF2/CF2	60	31	78
OF3/CF3	21	13	55
OF4/CF4	57	22	12

TABLE 2 : Conversion ratio under steady-state illumination of OF in dioxan, and hyperpolarisabilities of both OF and CF measured at 1.907 μm in dioxan.

μβ values show, except for OF5/CF5, a rather large increase by a factor of two to five in going from the open form to the closed form. The same increase was observed by Lehn and coworkers [3] for a push-pull diarylethene. However it is worthwhile to note that our compounds are symmetrically substituted, and have a structural similarity with Λ type molecules, rather than with linear push-pull molecules. For example, CF1 is of DAD type, with two p-anisyl donating (D) groups and one perfluorocyclopentyl attracting (A) group. Calculations of μ and β have been made for OF1 and CF1 with the MOPAC package, using the semi-empirical AM1 method to minimize energy, and a finite field algorithm to determine β (at zero frequency). Taking into account both parallel and antiparallel conformers, the calculated products $\mu\beta$ have been found equal to 26.7 10^{-48} esu for OF, and 47.52 10^{-48} esu for the closed form. This increase by a factor of two is much less than the observed one (see Table 2) and mainly comes from a large discrepancy between the observed and the calculated $\mu\beta$ values for the closed form. Although the SHG signal was out of the absorption band, we know that the two-level model is useless in the case of Λ shape molecules to predict a dispersion factor. Furthermore, in agreement with the Λ shape of the molecules, calculations have shown that there is a non diagonal predominating term in the β tensor, which is β_{yxx} in the case where the molecule CF1 lies in xOy plane, with Oy as the C_2 symmetry axis.

Photoswitching of the SHG signal of a PMMA/ dithienylethene film

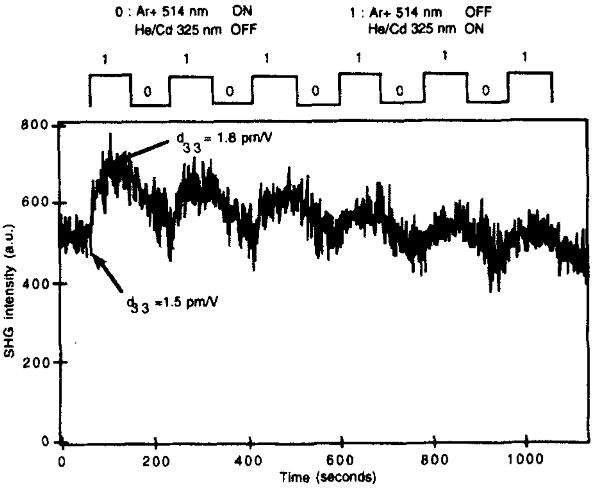


FIGURE 1 : Photomodulation of the SHG signal (fundamental at 1.064 μm) for a PMMA film doped with OF1 (10 % w/w) under succesive irradiations at 325 nm and 514 nm.

Photomodulation of the SHG signal during alternate irradiation with visible and UV light has already been demonstrated for spiropyran/photomerocyanine[9] and for Aberchrome [9][10]. Dithienylethenes seem promising, as the change in geometry during the photochromic reaction is small and could prevent disorientation .

This preliminary experiment shows a photomodulation of the SHG signal measured at 532 nm, with an increase during ring closure and a decrease during ring opening, in agreement with our prediction. Unfortunately, as in other polymer films, there is an irreversible decay of the overall SHG signal which is due to the loss of polar order in the film.

CONCLUSION

Dithienylethene derivatives present molecular NLO properties that can be switched by light between different values depending on the extent of delocalization . However, a lot of work is still needed in order to find solid state systems in which completely reversible photomodulation of the SHG signal can be effected. Because of the bistability of orientation, photochromic crystals seem promising in this respect.[11]

References

[1] Y. Atassi, J. Chauvin, J.A. Delaire, J.F. Delouis, I. Fanton-Maltey, K. Nakatani, *Pure and Appl. Chem.* **70,** 2157 (1998).

[2] Y. Atassi, J. Chauvin, J.A. Delaire, J.F. Delouis, I. Fanton-Maltey, K. Nakatani, *Mol. Cryst. Liq. Cryst.* **315,** 11 (1998).

[3] S.L. Gilat, S.H. Kawai, J.M. Lehn, *Chem. Eur. J.* **1,** 275 (1995).

[4] I. Maltey, J.A. Delaire, K. Nakatani, P. Wang, X. Shi and S. Wu, *Advanced Materials for Optics and Electronics* **6,** 233 (1996).

[5] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, *J. Org. Chem.* **60,** 8305 (1995).

[6] M. Irie, M. Mohri, *J. Org. Chem.* **53,** 803 (1988).

[7] H. Hanazawa, R. Sumiya, Y. Horikawa, M. Irie, *J. Chem. Soc. Chem. Com.* 206 (1992).

[8] M. Irie, O. Miyatake, K. Uchida, *J. Am. Chem. Soc.* **114,** 8715 (1992).

[9] Y. Atassi, J.A. Delaire and K. Nakatani, *J. Phys. Chem.* **99,** 16320 (1995).

[10] K. Nakatani, Y. Atassi and J.A. Delaire, *Nonlinear Optics,* **15,** 351 (1996).

[11] K. Nakatani and J.A. Delaire, *Chem. Mater.* **9,** 2682 (1997).