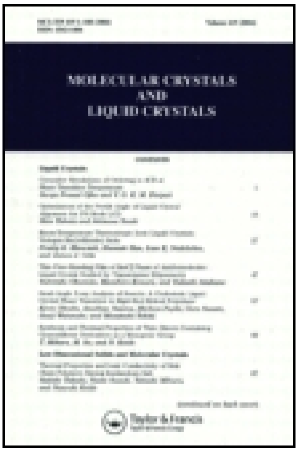

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Light Induced Changes in NO 2 -Substituted Rotaxanes: Switching Behavior in Mechanically Interlocked Architecture

V. Bermúdez [a] , P.-A. Chollet [a] , F. Kajzar [a] , A. Lorin [a] , G. Bottari [b] , F. G. Gatti [b] & D. A. Leigh [b]

[a] DECS/SE2M/LCO CEA Saclay, LIST (CEA - Recherche Technologique), Gif-Sur-Yvette Cedex, 91191, France

[b] Centre for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Coventry, CV4 7AL, UK

Version of record first published: 29 Oct 2010

To cite this article: V. Bermúdez, P.-A. Chollet, F. Kajzar, A. Lorin, G. Bottari, F. G. Gatti & D. A. Leigh (2002): Light Induced Changes in NO 2 -Substituted Rotaxanes: Switching Behavior in Mechanically Interlocked Architecture, Molecular Crystals and Liquid Crystals, 374:1, 343-356

To link to this article: http://dx.doi.org/10.1080/713738236

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 343-356
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1058-725X/02 $12.00 + .00

Light Induced Changes in NO_2-Substituted Rotaxanes: Switching Behavior in a Mechanically Interlocked Architecture

V. BERMÚDEZ[a,*], P.-A. CHOLLET[a], F. KAJZAR[a], A. LORIN[a], G. BOTTARI[b], F. G. GATTI[b] and D. A. LEIGH[b]

[a]*LIST (CEA - Recherche Technologique), DECS/SE2M/LCO CEA Saclay, 91191 Gif-Sur-Yvette Cedex, France and*
[b]*Centre for Supramolecular and Macromolecular Chemistry, Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK.*
[*]*Present address: Dpto. Física de Materiales, Universidad Autónoma de Madrid, 28049 Madrid, Spain*

ABSTRACT

Linear and nonlinear optical properties of thin films of pure fumrot, and mono -, as well as di – substituted with nitro group, rotaxanes were studied by m-lines spectroscopy and by third harmonic generation techniques, respectively. The molecules form, transparent in visible, good optical quality thin films by vacuum sublimation. The as deposited films exhibit, depending on substitution, optical birefringence. At 1.907 μm fundamental wavelength the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility varies between $(1.990\pm0.007)\text{x}10^{-12}$ esu (pure fumrot) and $1.809(\pm0.006)\text{x}10^{-12}$ esu (di-substituted). The light illumination in the rotaxane absorption band leads to a reversible modification of the optical absorption spectrum and is associated at the same time with a decrease of the cubic susceptibility. The THG susceptibility recovers its initial value after a few days. The largest variation is observed in pure fumrot.

Keywords: rotaxanes; third harmonic generation, photoisomerization

INTRODUCTION

At present time there is a great interest in the design and the synthesis of new, addressable, functional organic molecules for use in various types of practical applications. Mechanically-interlocked hydrogen bond assembled rotaxanes are organic systems which offer unique architectural and structural properties [1,2]. Current high yielding methods to prepare interlocked molecular structures are inspired by the pioneering works of Sauvage [3] and Stoddart [4]. Rotaxanes are a class of mechanically interlocked molecules where a macrocyclic ring is locked onto a thread by two bulky stoppers [5] (cf. Fig. 1). They have attracted great attention as promising candidates for the development of prototypical structural units for device applications because macrocycles can rotate and translate back and forward along the chain. Rotaxane architectures are thus particularly attractive because the components of the molecule are held together by a dynamic mechanical bond which can be controlled at the molecular level by applying an external stimuli [6]. Rotaxanes have been proposed as nanoscale devices such as switchable molecular brakes [3], shuttles [7], ratches [8] and electronically configurable logic gates [9]. Moreover the absence of chromophores or redox sensitive groups make rotaxanes an ideal backbone onto which additional electro-optically active sub-units can be assembled to form a new type of interlocked artificial functional materials for useful electronic or optical properties.

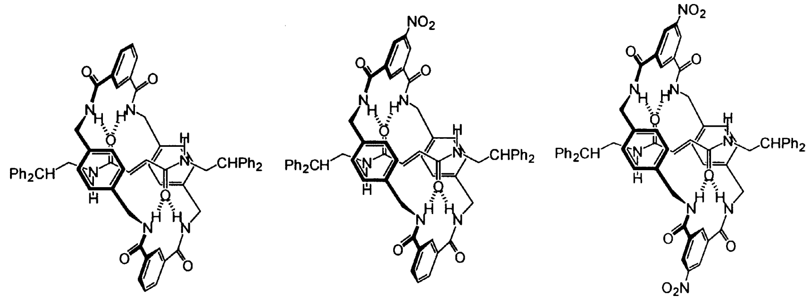
Dynamics of the mechanical bonds linking the ring, the thread and the stoppers, components of the rotaxane compounds, occupies a special place due to the specific degrees of freedom they have. These degrees of freedom, not available in other materials, can be used to switch the molecular properties through the adequate changes in the local environment, chemical stimuli and external optical or electrical applied fields [10] – [11].

Benzylic amide-rotaxanes (cf. Fig. 1) form a family of newly synthesized compounds which appear to be an ideal backbone onto which functional groups and subunits can be attached and the dynamic properties of rotaxanes exploited to get artificial materials with useful electronic or optical properties. This new class of compounds may be very attractive for device applications and, in particular, in optical switching.

In this work we show an experimental evidence of the influence of the NO_2 substituted groups in the rotaxane macrocycle on the linear optical properties and switching behavior of rotaxanes under UV irradiation in their absorption band.

MOLECULES

Rotaxanes were synthesized by the "clipping" methodology, consisting on the simultaneous slow addition of solutions of isophthaloyl dichloride and p-xylylene diamine in chlorinated solvents in the presence of the respective threads, with triethylamine as base. The thread provides the template information to form the benzylic amide macrocycle around itself via intermolecular hydrogen bond interactions (efficiency was more than 97% in the formation reaction, indicating close complementarity between the macrocycle and the thread). The three rotaxanes have the same fumaric thread while macrocycle differs from pure fumrot **1** in the addition of one nitro group in the case of mono-nitro fumrot **2** and two nitro groups in the case of di-nitro fumrot **3** as shown in Figure 1.



1 **2** **3**

FIGURE 1 Chemical structure of studied rotaxanes.

THIN FILM DEPOSITION AND LINEAR OPTICA PROPERTIES

Thin films of each rotaxane were deposited on fused silica and glass slides by vacuum sublimation. The vacuum level during deposition was 10^{-6} Torr, the powder and target temperatures were 220°C and 25°C respectively, and the deposition rate was varied from 100Å/s at the beginning of the procedure to 10-15 Å/s after the first 100 nm thickness was obtained and then until the end of the process.

The absorption spectra of thin films were recorded in transmission by using a Perkin Elmer Lambda 19 spectrophotometer and are shown in Fig. 2. The thickness of the studied thin was determined by the profilometric technique and was found to be 0.7099 μm, 0.362 μm and 0.198 μm for rotaxanes **1**, **2** and **3,** respectively. The optical absorption spectra of thin films, shown in Figure 2, are normalized to the same thickness. The main peak for **1** is not visible because of the absorption of fused silica beyond 200nm. A little shoulder of the main band is present at the wavelength of about 220 nm. For rotaxane **2** the main peak is located at about 230 nm and a little absorption band is located at about 275 nm. Rotaxane **3** reproduces the location of the peaks of rotaxane **1** with an increase in the optical density associated to them.

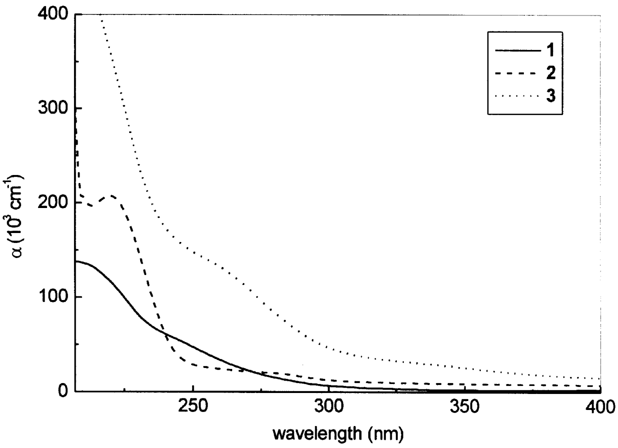


FIGURE 2 Optical absorption spectra of rotaxanes **1**, **2** and **3**. The spectra are normalized to the same thin film thickness.

The optical density increases with the number of NO_2 groups in macrocycle. The main fact that can be noticed from the optical absorption spectra is that there exists a shift in the peaks position of rotaxane **2** probably induced by a change in the refractive index due to asymmetry in the macrocycle created by the addition of only one NO_2 group.

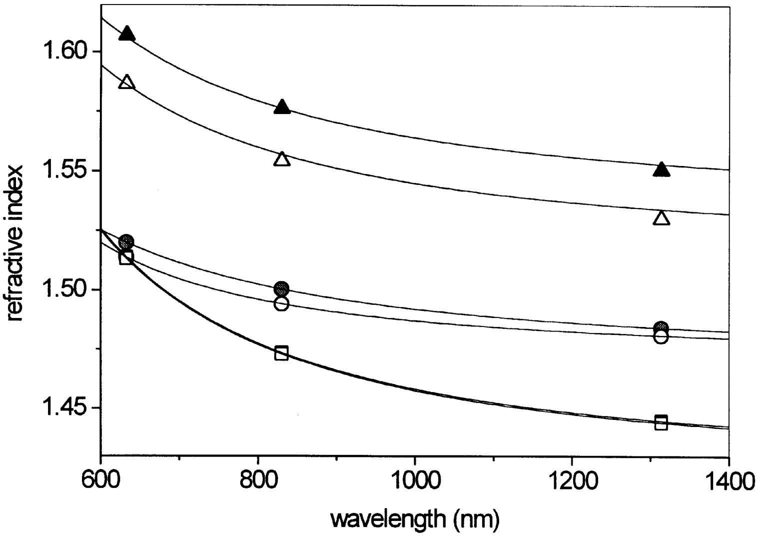


FIGURE 3 Wavelength dependence of refractive index in the studied crotaxanes. Triangles, circles and rectangles show experimental points for rotaxanes 1, 2 and 3, respectively. Open marks denote TM while closed the TE refractive index. Continous lines in Fig. 4 depict fitted values using the Sellmeier equation (Eq. 1).

The refractive indices of rotaxane thin films were measured in the visible and near infrared, at 623.8nm, 830nm and 1314nm, by means of m-lines spectroscopy. This technique allows to measure both the refractive index and the thickness when the films support more than one guided mode. It allows also to measure the optical birefringence by choosing the adequate polarization of the coupled light into thin film. Figure 3 shows the measured wavelength dependence of refractive indices of studied rotaxanes for TE and TM polarization. A large optical birefringence is observed in thin films of pure fumrot (**1**, Fig. 1). The attachment of the nitro group to macrocycle results in a decrease of the order in the case of mono substituted rotaxanes and its disapparence for the di-substituted one. In the last case the obtained thin films are almost isotropic. This behavior shows influence of the nitro group on the growth of thin films and the order.

The measured refractive indices were fitted by the Sellmeier equation:

$$n^2(\lambda) = A^2 + \frac{B}{\lambda^2 - C^2} \tag{1}$$

where λ is wavelength in nm. The values for A, B and C parameters for unpoled films for TE and TM polarizations are listed in Table 1. The values for thin film thickness obtained from m-line spectroscopy measurements were close to those determined by profilometric techniques (within 10%).

Table 1

Fit parameters of Sellmeier equation (Eq. (1)) to refractive indices of studied rotaxane films.

Rotaxane	**A**	**B(nm^2)**	**C(nm)**	**A**	**B(nm^2)**	**C(nm)**
FUMROT	1.5383	76728.1	201.01	1.5199	7353.85	208.2
MONOFUMROT	1.4278	80511.19	286.99	1.4268	81542.55	282.15
DIFUMROT	1.4735	53967.54	114.74	1.4735	36210.39	317.33
	TE modes			**TM modes**		

THIRD HARMONIC GENERATION MEASUREMENTS

The THG measurements were performed with a 10-pps Q-switched Nd:YAG laser at 1.907 μm fundamental wavelength; obtained by the

Raman shift (first Stoke radiation) of 1.064 μm in a high pressure (56 bar) hydrogen cell. The pulse duration was 13 ns. A detailed description of the experimental set-up is given in Ref. [12]. All THG measurements were performed under vacuum in order to avoid environmental effects [13]. The THG signal was independently calibrated with THG from a graded silica slab with a known nonlinear optical response [14]. For the experimental evaluation of the third order electronic susceptibility $\chi^{(3)}$, the THG intensities were measured as a function of the incidence angle θ by rotating thin films, which were mounted in a goniometer placed on a rotating stage.

In general the resultant harmonic field at the output of a nonlinear medium is a superposition of harmonic fields generated in different points. For the case considered here (thin films deposited on a transparent silica substrate placed in a vacuum chamber), only harmonic fields generated in the substrate and in the thin film contribute to the measured signal. Assuming that the thin film is on the PMT side, the resultant harmonic intensity is given by the following expression ([12], [15])

$$I_{3\omega}(\theta)=\frac{64\pi^4}{c^2}\left|\left(\frac{\chi^{3/}}{\Delta\varepsilon}\right)_s e^{-i\left(\varphi_\omega^s+\varphi_{3\omega}^f\right)}\left[T_1\left(1-e^{-i\Delta\varphi_s}\right)+\rho T_2 e^{i\Delta\varphi^s}\left(e^{-i\Delta\varphi_f}-1\right)\right]\right|^2 (I_\omega)^3 \tag{2}$$

where T_1 and T_2 are factors arising from transmission and boundary conditions for electric and magnetic fields as defined in Refs. 12 ,13 and 15

$$\Delta\varphi=\varphi_\omega-\varphi_{3\omega}=3\omega\ \left(n_\omega\cos\theta_\omega-n_{3\omega}\cos\theta_{3\omega}\right)/c \tag{3}$$

is the phase mismatch between the fundamental and the harmonic frequencies, where θ_ω and $\theta_{3\omega}$ are propagation angles at ω and 3ω frequencies (for details see Ref. [12]) and I_ω is the fundamental beam intensity. $\rho=\frac{\left(\chi^{3/}/\Delta\varepsilon\right)_f}{\left(\chi^{3/}/\Delta\varepsilon\right)_s}$ is the ratio of the cubic susceptibilities of the film (f) and the substrate (s) both normalized to the dielectric constant dispersion $\Delta\varepsilon=\varepsilon_\omega-\varepsilon_{3\omega}$. $n_{\omega(3\omega)}=\varepsilon_{\omega(3\omega)}^{1/2}$ are the refractive indices; c is the speed of the light. The thin film absorption is taken into account by introducing complex refractive index in Eq. (2).

The modulus of the nonlinear optical susceptibility of rotaxane thin film can be determined from Maker fringes by fitting Eq. (2) to experimental data as shown in Figure 4. The optical pathlength variation between neighboring minimum and maximum intensity is equal to the coherence length $l_c = \frac{\lambda_\omega}{6(n_{3\omega} - n_\omega)}$. The THG intensity was calibrated by performing independent measurements on silica substrate alone, done at the same conditions. The dielectric dispersion $\Delta\varepsilon_S$ and the cubic susceptibility of fused silica ($\chi^{(3)} = 2.8\text{x}10^{-14}$ esu at 1.907μm) were taken from Ref. 14. Equation (2) holds for any thin film thickness. However, in the case of absorbing films, the thickness should be sufficiently small in order to assure a nonextinction of the

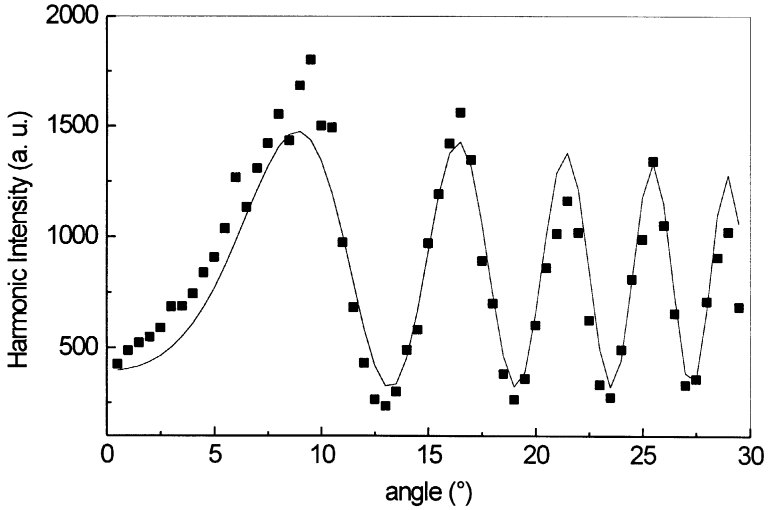


FIGURE 4. Maker fringes corresponding to the angular variation measurement of the harmonic intensity for **2** at 1.907μm. Dots are experimental points and continuos line shows the theoretical fitting to Eq. (2) in text.

free wave. In our case no rotaxane is absorbing at third harmonic frequency of 1.907 μm.

RESULTS

Thin film homegeneity and photoisomerization studies

The homogeneity of the studied thin films was verified by doing THG measurements when translating the film perpendicular to the beam propagation direction. This is a quite sensitive technique as THG intensity varies proportional to the square of the thin film thickness. The observed almost constant THG intensity as function of translation is a proof of the good thin film homogeneity.

In the threads is present a C=C bond (cf. Fig. 1) which illuminated in its absorption band may lead to a change of molecule conformation through *trans-cis* and *cis-trans* isomerization process. Such change of conformation is associated with the variation of the conjugation length and consequently a shift in the optical absorption spectrum. As NLO response depends strongly on the conjugation length a variation in $\chi^{(3)}$ susceptibility should be observed when passing from one form to another one. The trans form shows a better conjugation and exhibits a smaller optical gap. Depending on molecule environment such transformations not always are possible. Also transformation from trans to cis form may be irreversible or partial. Usually the trans form absorbs in the range 300-400 nm, while the cis form below. In order to check such possible variations, which are important for applications of these molecules as switching elements or as molecular motors two kind of experiments were done :

(i) monitoring with time of linear absorption spectrum after UV irradiation
(ii) similar *in situ* study of cubic susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$

Thin films of rotaxanes were irradiated with a mercury lamp, equipped with an interference filter, centered around 350 nm. As example, Figure 5 shows the observed variation of the optical absorption spectra of rotaxane **1**. The same behavior takes place also in the case of rotaxane **2**. Contrariwise, the absorption spectrum of rotaxane **3** does not change under UV irradiation. As it can be seen from Fig. 5 , due to the UV illumination, the edge of optical absorption shifts to lowe wavelengths inmediately after irradiation, as it is usually observed in the trans-cis isomerization process.

The optical density of the material also decreases. The recovery in the absorption spectra is quite slow when stopping illumination. Only 1 day after irradiation the absorption spectra have recovered totally their initial shape.

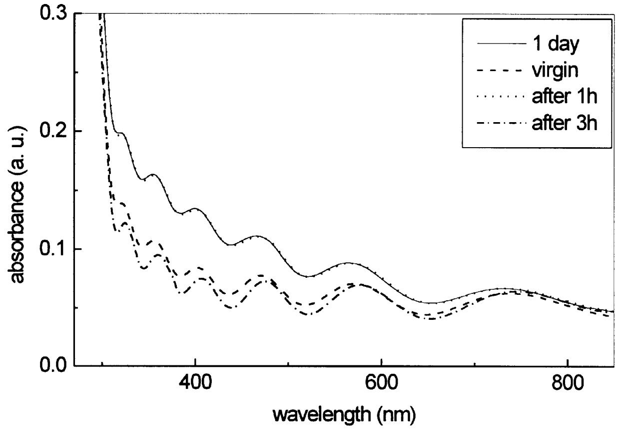


FIGURE 5. Optical absorption spectra of rotaxane **1** before and several times after UV irradiation.

From the interference patterns observed in the absorption spectrum of thin films (cf. Fig. 5) it is possible to calculate the change in the medium refractive index with time after UV irradiation using the following equation:

$$m = \frac{\lambda_m \pm 1}{\lambda_m - \lambda_{m\pm 1}} \tag{4}$$

where λ_m and λ_{m+1} are the corresponding values of wavelengths λ corresponding to two adjacent interference extrema. By knowing the film thickness and using equation:

$$d = \frac{m\lambda_m}{4n} \tag{5}$$

one gets the corresponding refractive index change Δn at given wavelength. For interference patterns shown in Figure 5 the calculations give Δn ~ 0.017±0.008; 0.0099±0.0009; 0 for elapsed time 1 h, 3 h and 1 day, respectively. It is important to note that after 1 day the absorption spectrum is completely recovered and there is no photoinduced damage.

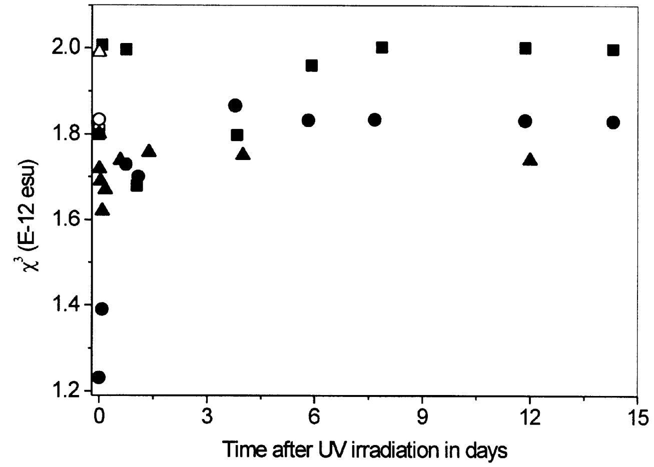


FIGURE 6 Temporal evolution of $\chi^{(3)}$ susceptibility as measured by THG for three rotaxanes. Open symbols denote the corresponding values before irradiation. The symbols , O, and Δ refer to rotaxanes **1**, **2** and **3** respectively.

THG measurements

From Fig. 2 it is seen that rotaxanes are transparent at fundamental and harmonic wavelength for 1.907 μm fundamental wavelengths, so we can not expect resonant enhancement in $\chi^{3)}$ due to the presence of an excited state at one of these wavelengths.

Similarly as in the study of optical absorption variation the rotaxane films were irradiated with an UV lamp during the THG measurements at 1.907μm fundamental wavelength. As already mentioned the observed previously variation of the conjugation length and its decrease due to irradiation should be accompanied by a decrease of THG susceptibility. Indeed, as it is seen from Figure 6, immediately after irradiation one observes a significant decrease of $\chi^{(3)}$ susceptibility and its slow recovery when UV irradiation stops. As it is seen from Fig. 6 the highest value of the third-order NLO susceptibility is measured in rotaxane **1** while rotaxanes **2** and **3,** within experimental accuracy, exhibit almost the same value,. It is worth noting that the strongest decrease in $\chi^{(3)}$ susceptibility, due to UV irradiation, is observed in rotaxane **2** . This change in the THG susceptibility is completely recovered after 6-9 days indicating that the molecule is not damaged by UV irradiation. Rotaxane **1** is slightly affected with UV irradiation and although it recovers after 9 days some damage is observed, as it is seen from the lower value of $\chi^{(3)}$ after several days. Rotaxane **3** does not change, within experimental error, after UV irradiation. The mesured values of third-order NLO susceptibility for rotaxanes **1**, **2** and **3** before UV irradiation are $(1.99 \pm 0.007) \times 10^{-12}$ esu, $(1.834 \pm 0.004) \times 10^{-12}$ esu and $(1.809 \pm 0.006) \times 10^{-12}$ esu, respectively.

The observed evolution in $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility under UV illumination is another proof of the change in the conjugation length of studied rotaxanes, which is due to the photoizomerization process. We note that the sensitivity of NLO susceptibility to the conjugation length variation is higher than that of linear optical absorption spectrum, where the picture can be screened by possible photochemical damage. The fact that only 6-9 days after irradiation we recover the initial NLO susceptibility for rotaxane **2** shows reversibility of the process as well as its connection to the variation of the conjugation length as in trans-cis isomerization, although a photoinduced damage to the molecule may occur. The observed variation of the conjugation length is very slow. This is due to the limited mobility of the thread in solid film. It shows also clearly that the photoisomerization process depends on molecule structure. We note here that only that only in rotaxane **3** a photodegradation occurs under UV irradiation.

CONCLUSIONS

We have studied the linear and nonlinear optical properties of a series of 3 rotaxanes: pure fumrot as well as mono -, di – substituted with nitro group NO_2. The studied rotaxanes can be processed into good optical quality thin films by vacuum sublimation method. The refractive indices of thin films were determined by m-lines technique. As deposited films exhibit quite large birefringence. This birefringence depends on the substitution: the largest is observed in the case of pure fumrot, whereas the di-substituted fumrot forms almost isotropic thin films. It shows influence of substitution on the formation ordered thin film.

Thin films illuminated within the UV absorption bands exhibit a reversible, slow, photoisomerization process. This illumination leads to a permanent damage in the case of rotaxane 3. It shows that the chemical structure plays an important rôle in photostability of organic molecules.

The nonlinear optical properties of rotaxane thin films were studied by the optical third harmonic generation technique. At 1.907 μm fundamental wavelength the $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ susceptibility varies between (1.990±0.007)x10^{-12} (pure fumrot) and (1.809±0.006)x10^{-12} esu (di-substituted fumrot). It shows infuence of substitution on third-otrder NLO sussceptibility.

The light illumination in the rotaxane absorption band leads to a reversible modification of the optical absorption spectrum and is associated at the same time with a decrease of the cubic susceptibility. The THG susceptibility recovers its initial value after a few days. The largest variation is observed in pure fumrot.

ACKNOWLEGDEMENTS

This work was supported by the European community under TMR contract : ERB4061PL95-0968 (ENBAC, A European Network on Benzylic Amide Catenanes).

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