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Nonlinear optical properties of a new stable ferrocenyl Schiff-base polychlorotriphenylmethyl radical

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Abstract

Here we report the NLO properties of the isomeric *trans* and *cis* forms of radical **1**. This fact allowed us to prove the feasibility of polychlorotriphenylmethyl radicals as building blocks with electron acceptor ability for NLO materials. Moreover, by comparing the β_{vec} values obtained for isomers *trans*-**1** and *cis*-**1** with those of related ferrocenyl-based chromophores, we propose that molecular torsions strongly decrease the second-order NLO response.

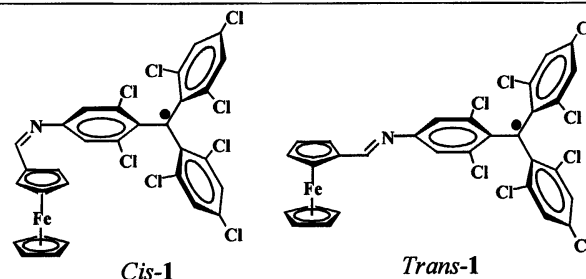
Keywords: Triphenylmethyl radical, *cis-trans*, nonlinear optics

1. Introduction

In the last few years, a large interest has been devoted to the investigation and development of NLO materials having *open-shell* electronic structures. As it has been recently pointed out,¹ species having *open-shell* electronic states, such as organic radicals, can exhibit very large first-order hyperpolarizability (β) in comparison with analogous *closed-shell* systems, thanks to the presence of accessible low-lying charge transfer electronic states. Despite this fact, scant examples of organic *open-shell* species showing NLO responses have been reported, mostly due to the inherent low persistency and large photo-optical instability of these species.²

For this reason, we focussed our attention in the synthesis and characterization of new NLO materials using polychlorinated triphenylmethyl (PTM) radical units as building blocks. The interest for these radicals is twofold. First, their low reduction potentials indicate that they may act as effective electron acceptor units. Second, these radicals have their *open-shell* centers sterically shielded by six bulky chlorine atoms in order to increase their life expectancies and thermal and chemical stabilities.³

In a previous communication we reported the possibility to synthesize, isolate and characterize the *trans* and *cis* isomers of the ferrocenyl schiff-base polychlorotriphenylmethyl radical (**1**).⁴ In this communication, we report for the first time the NLO properties of both isomeric forms, *trans*-**1** and *cis*-**1**.



2. Experimental

Compounds *trans*-**1** and *cis*-**1** were obtained as previously described. $\mu\beta$ values were measured with a nonlinear optics spectrometer from SOPRA S.A. The fundamental source at 1907 nm came from the first Stokes peak of a hydrogen Raman cell pumped by the 1064 nm light of a Q-switched Nd:YAG laser (Quatel YG 781, 10 pps, 8 ns pulse). The resulting beam light was passed through a linear polarizer and focused on the EFISH cell. The applied DC electric field (parallel to the light polarization) was 7 kV. The output light of the cell was passed through an interference filter to select the second harmonic light, which was detected with a R642 photomultiplier from Hamamatsu. All the experiments were carried out in CH_2Cl_2 irradiating at $\lambda = 1907$ nm. μ values were calculated from the minimized ZINDO/1 structures.

3. Nonlinear optical properties

Donor-Acceptor systems are one of the most developed structures in the search for new compounds with efficient

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NLO responses.⁵ *Trans*-1 and *cis*-1 fulfill such a donor-acceptor structure, where the ferrocene is acting as a donor unit, the triphenylmethyl radical is acting as an acceptor unit, and both are connected through a conjugated $-\text{CH}=\text{N}-$ bridge. This is the first example of a NLO material that combines an *open-shell* organic radical as the acceptor unit and a ferrocene moiety as the donor group. The synergism of both units was expected to drastically increase the NLO of such a material.

In agreement with our expectancies, attachment of an organic radical acceptor to the ferrocene unit results in the observation of a second-order NLO response. The β_{vec} values found for *trans*-1 and *cis*-1 isomers are shown in Table 1.

Table 1.
NLO properties of *trans*-1 and *cis*-1

	λ_{max} (nm) ^a	$\mu\beta \cdot 10^{-48}$ esu	$\mu \cdot 10^{-18}$ esu	$\beta \cdot 10^{-30}$ esu
<i>Cis</i>	566	100	7,92	12,6
<i>Trans</i>	563	106	8,38	12,6

As far as we know, compound 1 is the second radical-based chromophore whose second-order NLO properties have been measured using the EFISH technique. The first one was the pure organic *p*-nitrophenyl α -nitronyl nitroxide radical, described by Zyss *et al.*,⁶ which gave a β_{vec} value of 6.24×10^{-30} esu. On the other hand, the β_{vec} values found for *trans*-1 and *cis*-1 isomers closely resemble those previously reported for similar ferrocene-based chromophores of the form $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)-(\text{CH}=\text{CH})-p\text{-C}_6\text{H}_4\text{-Y}$, where Y stands for groups of different acceptor strength capacities.⁷ Thus, the expected synergic behavior in the combination of ferrocene donor and PTM acceptor does not appear in compound 1. This fact may arise from the presence of unexpected molecular torsions, which disturb the coplanarity of the molecular systems. In order to assess such possibility, ZINDO/1 semiempirical calculations were used. The ZINDO/1 minimized geometry of both isomers show a strong torsion between the phenyl unit and the $\text{C}=\text{C}=\text{N}-\text{C}$ plane making a dihedral angle of 55° . To better illustrate this fact the ZINDO minimized structure of isomers *trans*-1 and *cis*-1 are shown in Fig. 1.

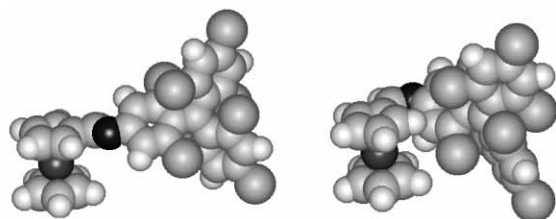


Fig. 1. *Trans*-1 and *cis*-1 minimized structures using a semiempirical ZINDO/1 method.

Such torsion probably arises from the overlap between the lone pair electrons on the nitrogen and the π system of the

phenyl ring. The lack of coplanarity leads to a poor π conjugation in the system and, therefore, to the obtaining of lower β_{vec} values than those initially expected. The same arguments can be used to explain the similar β_{vec} values found for the isomeric forms, *trans*-1 and *cis*-1, while considerable differences between the second-order NLO responses of two isomers were expected.⁷

4. Conclusions

In summary, we have reported the second-order NLO properties of compounds *trans*-1 and *cis*-1. This fact allowed us to prove the feasibility of polychlorotriphenylmethyl radicals as building blocks with electron acceptor ability for NLO materials. Moreover, by comparing the β_{vec} values obtained for isomers *trans*-1 and *cis*-1 with those of related ferrocenyl-based chromophores, we propose that molecular torsions strongly decrease the second-order NLO response. Further studies directed towards the synthesis and characterization of new ferrocene-based organic radical chromophore are being pursued nowadays in our laboratory. Such ferrocene-based organic radical chromophore use an ethylene bridge, which is expected to give rise to a more coplanar structure and therefore to an enhancement of the NLO properties of this kind of materials. The use of a nonamethylated ferrocene unit is also expected to enhance the NLO properties of the system thanks to its higher donor ability.

This work was supported from DGES (PB96-0862-C02-01), CIRIT (1998SGR-96-00106), the 3MD Network of the TMR program of the E.U. (contract ERBFMRXCT 980181) and CICYT (Project MAT-99-1009-C02-01). D. R.-M. is grateful to the Generalitat de Catalunya for a postdoctoral grant and I. R. is grateful to a CSIC-Carbueros Metálicos for a fellowship.

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