

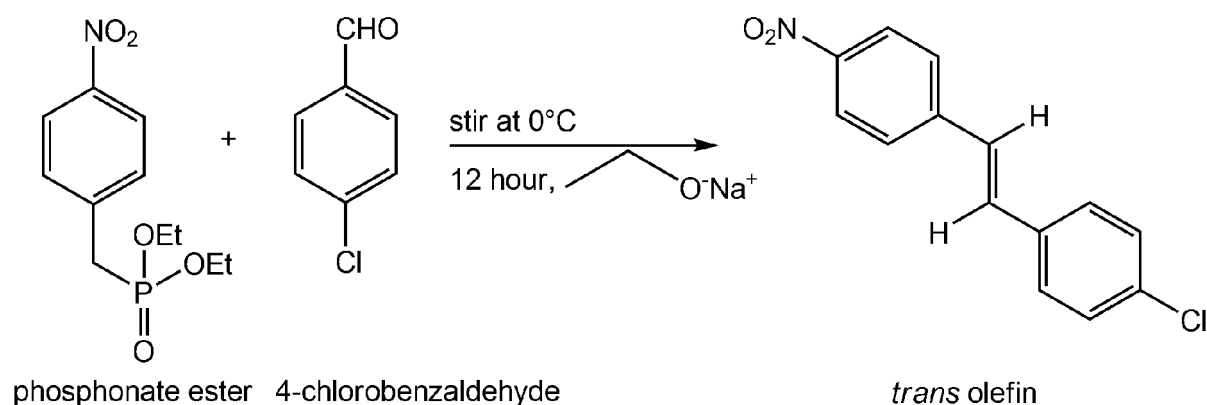
Published in: Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy: 117; 2014; 817-819.

Comment on the paper 'Synthesis, growth, structural, spectral, thermal, chemical etching, linear and nonlinear optical and mechanical studies of an organic single crystal 4-Chloro 4-Nitrostilbene (CONS): A potential NLO material' by P.M. Dinakaran, S. Kalainathan, Spectrochim. Acta A111 (2013) 123-130

Bikshandarkoil R. Srinivasan, Sunder N. Dhuri, V.S. Nadkarni
Department of Chemistry, Goa University, Goa 403206, INDIA

Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184

Graphical Abstract



Published in: Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy: 117; 2014; 817-819.

Highlights

- (*Trans*)-4-chloro-4'-nitrostilbene is not a novel organic NLO single crystal.
- (*Trans*)-4-chloro-4'-nitrostilbene is an yellow crystalline solid.
- Organic chloro compounds exhibit characteristic mass spectra.

Published in: Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy: 117; 2014; 817-819.

Comment on the paper ‘Synthesis, growth, structural, spectral, thermal, chemical etching, linear and nonlinear optical and mechanical studies of an organic single crystal 4-Chloro 4-Nitrostilbene (CONS): A potential NLO material’ by P.M. Dinakaran, S. Kalainathan, Spectrochim. Acta A111 (2013) 123-130

Bikshandarkoil R. Srinivasan, Sunder N. Dhuri, V.S. Nadkarni
Department of Chemistry, Goa University, Goa 403206, INDIA

Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184
(V.S. Nadkarni) nitin@unigoa.ac.in Tel: 0091-(0)832-6519320; Fax: 0091-(0)832-2451184

Abstract

We argue that (*trans*)-4-chloro-4'-nitrostilbene is not a new organic nonlinear optical material as claimed by P.M. Dinakaran, S. Kalainathan, Spectrochim. Acta A111 (2013) 123-130, but instead a well-known compound whose synthesis, spectral data, single crystal structure and second harmonic generation (SHG) efficiency are well documented in the literature. The title paper is completely erroneous.

Keywords: (*trans*)-4-chloro-4'-nitrostilbene; nonlinear optical material; crystal structure; second harmonic generation; erroneous publication

1. Introduction

Contrary to the claim of the authors of the title paper [1] that they are reporting for the first time the details of the synthesis and characterization of (*trans*)-4-chloro-4'-nitrostilbene (**1**) by ¹H NMR, single crystal X-ray diffraction analysis, powder SHG test etc, (**1**) is a well-known yellow crystalline compound whose synthesis, spectral data, single crystal X-ray structure and SHG efficiency are well documented in the literature [2-9]. In this paper, the compound (*trans*)-4-chloro-4'-nitrostilbene is abbreviated as compound **1**, in order to avoid use of non-standard abbreviations like CONS. The reported spectral data in [1] are inconsistent for the ‘so called’ potential nonlinear optical (NLO) material (**1**) as will be shown in the following comment.

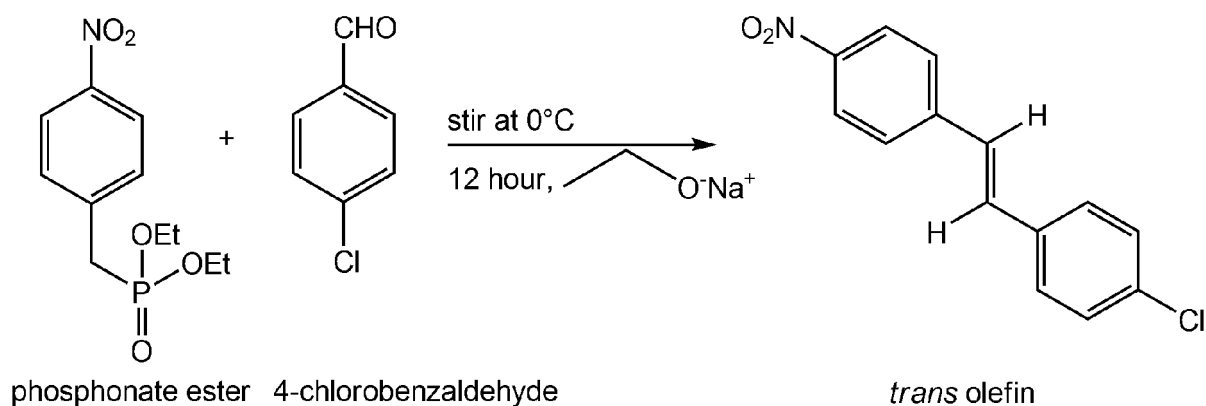
2. Comment

The synthesis of (*trans*)-4-chloro-4'-nitrostilbene **1** is known since the 1950's [2] and its ¹H NMR spectrum was first reported in 1967 [3] and more recently by Behrnd *et al* [7]. Wang *et al* reported the second harmonic generation (SHG) efficiency for **1** crystallized from different solvents [4] and the synthetic details and SHG characteristics of **1** were described in a patent titled, '*Nonlinear optical devices from derivatives of stilbene and diphenylacetylene*' [5]. In spite of such extensive literature on compound **1**, the authors of the commented paper begin their manuscript by claiming in the abstract '*4-Chloro 4-nitro stilbene (CONS) a new organic nonlinear optical material has been synthesized*'. Although the reason for this incorrect claim is not clear, it is noted that even the name of the compound under study was not written in accordance with IUPAC nomenclature. The correct name of **1** is used by us in this paper.

The research group of Hulliger has extensively investigated compound (**1**) [6-9] in recent years and have made some important contributions including the determination of its X-ray crystal structure and refining the same in the non-centrosymmetric Sohncke space group $P2_1$. Based on a very detailed X-ray analysis of weak superstructure reflections, these researchers showed that the crystal structure of (**1**) exhibits orientational disorder [6]. The authors of the title paper have cited this work of Behrnd *et al.* [6] (also Ref. 6 in the title paper), under the heading 'Single crystal XRD' while listing the unit cell data of the crystals. In spite of citing this work, the authors of the commented paper write in the introduction, '*In this paper we report for first time the details of the synthesis, growth and characterizations of CONS such as single crystal X-ray diffraction analysis, powder SHG test*'.

Many of the points mentioned in our recent comment on reports describing 4-substituted-4'-nitrostilbene compounds [10] are equally applicable for the characterization of **1** reported in the title paper. For example, the ¹H NMR data does not provide any information on the coupling constant (J_{HH} data in Hz) and the chemical shifts for the six different types of

protons in **1** are not assigned as per the normal practice [2, 7]. The correct NMR spectral data of **1** has been reported by Hulliger *et al* [7]. The claim of having performed X-ray single crystal structure determination is not substantiated with the refinement details, details of the structure model of **1** and a cif file. It is also not clear as to how (no mention of systematic absences) the authors could assign a monoclinic space group $P2_1$ without structure determination. The dubious nature of this single crystal X-ray can be evidenced by the fact that the value of Flack parameter [11] has not been assigned for the Sohncke space group. Although both single crystal and powder X-ray diffraction analyses were supposed to have been used for the characterization of **1**, it is not mentioned anywhere if the phenyl rings in **1** are disposed *cis* or *trans* to each other. For the synthesis of **1**, Hulliger *et al* [7] employed the well-known Horner-Wadsworth-Emmons (HWE) reaction protocol, which involves the reaction of 4-chlorobenzaldehyde with dimethyl(4-nitrobenzyl)phosphonate generated *in situ* in the presence of a strong base namely sodium ethoxide (Scheme 1). The same HWE protocol was used by the authors of the commented paper for the synthesis of **1**. The authors reacted commercially available diethyl(4-nitrobenzyl)phosphonate ester with 4-chlorobenzaldehyde in the presence of a base. However, the reported synthetic protocol is incorrect because the diethyl(4-nitrobenzyl)phosphonate ester is represented by a wrong structure [1]. The correct scheme for synthesis of **1** is given in Scheme 1.



Scheme 1. Reaction scheme for synthesis of (*trans*)-4-chloro-4'-nitrostilbene (**1**)

It is well documented that crystals of **1** are yellow in colour [4-9] unlike the green colored crystals grown by the authors of [1]. Crystals of **1** were recrystallized from ethyl methyl ketone by the authors of the commented paper unlike acetone or toluene used by Wang *et al* [4] and Hulliger *et al* [7] to get yellow crystals. No major difference should be expected in crystals grown from acetone or ethyl methyl ketone both of which are ketones and differ by a single methylene group. However the authors have not mentioned the reason for their choice of ethyl methyl ketone and the advantages offered by it over acetone for crystal growth.

The green color is not compatible with the yellow 4-substituted-4'-nitrostilbene chromophore [3-6, 8, 9], and can be attributed to the presence of some impurity phase in **1**. The presence of the *cis* isomer of **1** can be ruled out as an impurity because the HWE reaction is known to yield the *trans* olefin. It is well documented that organic chloro compounds exhibit characteristic mass spectra with the M and M+2 ions appearing as signals in the intensity ratio 3:1 [12]. However the reported mass spectrum appears abnormal indicating the presence of a mixture of compounds.

3. Conclusions

In summary, we have shown that the commented paper does not provide any new scientific information on the well-known compound (*trans*)4-chloro-4'-nitrostilbene, whose synthesis, X-ray structure and SHG properties are well documented in the literature [4-9].

References:

- [1] P.M. Dinakaran, S. Kalainathan, Synthesis, growth, structural, spectral, thermal, chemical etching, linear and nonlinear optical and mechanical studies of an organic single crystal 4-Chloro 4-Nitrostilbene (CONS): A potential NLO material Spectrochim. Acta A111 (2013) 123-130. <http://dx.doi.org/10.1016/j.saa.2013.03.048>
- [2] W. J. Dale, C. M. Ise, The Meerwein Reaction with p-Nitrostyrene and 2-Vinylpyridine, J. Am. Chem. Soc. 76 (1954) 2259–2260. <http://dx.doi.org/10.1021/ja01637a072>
- [3] H. Güsten, M. Salzwedel, Die kernmagnetischen resonanzspektren substituierter trans-stilbene, Tetrahedron 23 (1967) 173-185. [http://dx.doi.org/10.1016/S0040-4020\(01\)83298-1](http://dx.doi.org/10.1016/S0040-4020(01)83298-1)
- [4] Y. Wang, W. Tam, S.H. Stevenson, R.A. Clement, J. Calabrese, New organic non-linear optical materials of stilbene and diphenylacetylene derivatives, Chem. Phys. Letters 148 (1988) 136-141. [http://dx.doi.org/10.1016/0009-2614\(88\)80289-6](http://dx.doi.org/10.1016/0009-2614(88)80289-6)
- [5] R.A. Clement, W. Tam, Y. Wang, Nonlinear optical devices from derivatives of stilbene and diphenylacetylene, US Patent 4966730 (1990). <http://www.patentstorm.us/patents/4966730/description.html>
- [6] N.-R. Behrnd, G. Labat, P. Venugopalan, J. Hulliger, H.B. Burgi, Orientational Disorder of (trans)-4-Chloro-4'-nitrostilbene: A Detailed Analysis by Single Crystal X-ray Diffraction, Crystal Growth Des. 10 (2010) 52-59. <http://dx.doi.org/10.1021/cg801278j>
- [7] J. Hulliger, H. Bebie, S. Kluge, A. Quintel, Growth-Induced Evolution of Polarity in organic Crystals, Chem. Mater. 14 (2002) 1523-1529. <http://dx.doi.org/10.1021/cm010405y>
- [8] N.-R. Behrnd, G. Couderc, M. Wübbenhorst, J. Hulliger, Scanning pyroelectric microscopy revealing the spatial polarity distribution in topologically centric crystals of trans-4-chloro-4'-nitrostilbene Phys. Chem. Chem. Phys. 8 (2006) 4131-4137. <http://dx.doi.org/10.1039/B607409J>
- [9] N.-R. Behrnd, G. Labat, P. Venugopalan, J. Hulliger, H.B. Bürgi, Influence of the solvent of crystallization on the orientational disorder of (trans)-4-chloro-4'-nitrostilbene Cryst. Eng. Comm. 12 (2010) 4101-4108. <http://dx.doi.org/10.1039/b926652f>
- [10] B.R. Srinivasan, Z. Tylczyński, V.S. Nadkarni, Comment on 'Synthesis, growth, structural, spectral, linear and nonlinear optical and mechanical studies of a novel organic NLO single crystal 4-Bromo 4-Nitrostilbene (BONS) for nonlinear optical applications' Opt. Mater. (2013) <http://dx.doi.org/10.1016/j.optmat.2013.03.029>
- [11] H.D. Flack, Chiral and Achiral Crystal Structures, Helv. Chim. Acta 86 (2003) 905-921. <http://dx.doi.org/10.1002/hlca.200390109>
- [12] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley, Singapore, Fifth Edition (1991) 35-36.