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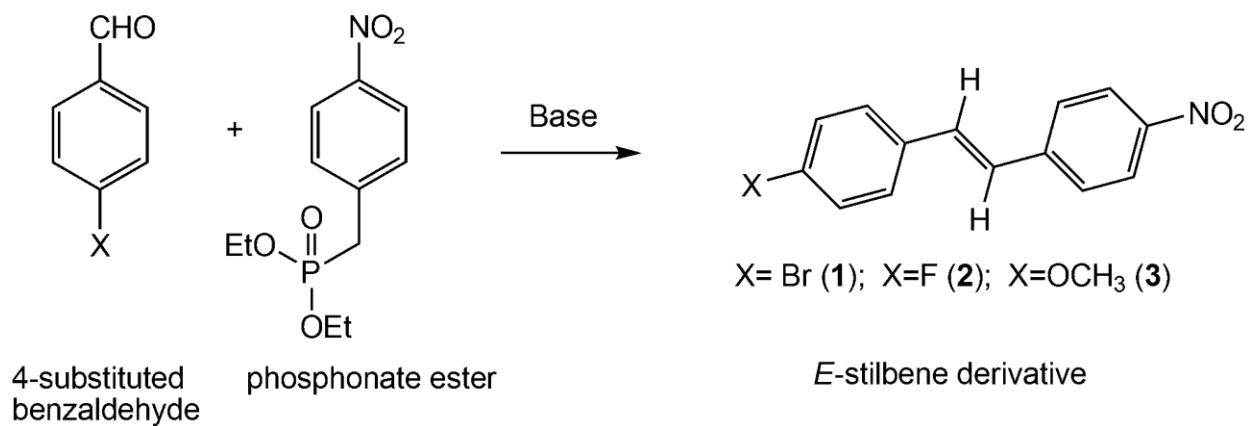
Comment on ‘Synthesis, growth, structural, spectral, linear and nonlinear optical and mechanical studies of a novel organic NLO single crystal 4-Bromo 4-Nitrostilbene (BONS) for nonlinear optical applications’

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Graphical Abstract



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’

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Abstract

We argue that the recently reported compound 4-bromo-4'-nitrostilbene (**1**) is not a novel organic NLO crystal as claimed by P.M. Dinakaran, S. Kalainathan, [Opt. Mater. 35, (2013) 898-903], but instead a well known compound whose characterization data and SHG efficiency are well documented in literature. The title paper is completely erroneous. Two more similar erroneous papers by the same authors are also commented.

Keywords: 4-bromo-4'-nitrostilbene; NLO crystal; SHG efficiency; dubious data.

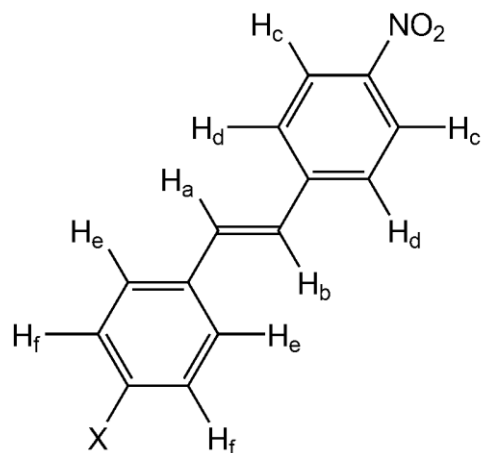
Introduction

In the rapidly expanding area of research on nonlinear optical (NLO) materials, several papers reporting on new non-centrosymmetric solids are being published. In addition to several valuable work, compounds which have not been properly characterized, are being published under the name new nonlinear optical (NLO) crystals and several such erroneous papers have been listed by Fleck and Petrosyan in a case study of NLO materials [1]. The title paper, in which the authors report the growth of 4-bromo-4'-nitrostilbene (**1**) as a novel organic NLO single crystal is one such erroneous report [2]. Two more papers by the same authors on 4-fluoro-4'-nitrostilbene (**2**) and 4'-methoxy-4-nitrostilbene (**3**) are also erroneous [3, 4]. The statement of authors of [2] that they are reporting for the first time the synthesis of

1 is incorrect, because **1** is a well-known compound [5-9]. The claim of the authors that compounds **2** and **3** [3, 4] are novel NLO materials is untenable as will be shown below.

Known chemistry of 4'-substituted-4-nitrostilbenes

Stilbene also known as diphenylethylene (PhHC=CHPh) is an unsaturated hydrocarbon. A stilbene containing a substituent (X) at the *para* position (4-substituted) of one of the phenyl rings and a -NO₂ group at the *para* position (4'-nitro) of the second ring is known as 4-substituted-4'-nitrostilbene. Compounds **1-3** differ in terms of the substituent X (X = Br **1**; X = F **2**; X = OCH₃ **3**) at the 4-position (Scheme 1). Depending on the disposition of the phenyl groups on either side of the double bond, a stilbene derivative can be classified as *cis* (*Z*)- or *trans* (*E*)-4-substituted-4'-nitrostilbene. Each one of the geometric isomers exhibits a characteristic coupling constant value for the two vinylic (-HC=CH-) protons in its ¹H NMR spectrum enabling its identification [10, 11]. In addition, the two sets of equivalent protons in each one of the phenyl rings exhibit characteristic chemical shifts. The synthesis, spectral characteristics and SHG properties of several stilbene derivatives including compounds **1-3** is well documented in the literature [5-16]. Wang *et al* showed a quarter century ago that the SHG efficiency of compounds **1-3** depends on the solvent from which the compound is crystallized [6]. It is interesting to note that the authors of [2] who did not cite the work of Wang *et al* [6], used the same abbreviation namely BONS for 4-bromo-4'-nitrostilbene **1** which incidentally was originally used by Wang *et al*. In a patent titled, 'Nonlinear optical devices from derivatives of stilbene and diphenylacetylene' Clement *et al* have described the synthesis and SHG characteristics of **1** and **2** [9]. In view of the above mentioned known results for **1-3**, it is not clear as to why the authors wrongly claim that the crystals grown and reported in [2-4] are novel organic NLO crystals. A scrutiny of these papers by the Kalainathan group reveals several inconsistencies indicating that the purity of the 'so called' novel compounds described in [2-4] is highly questionable.

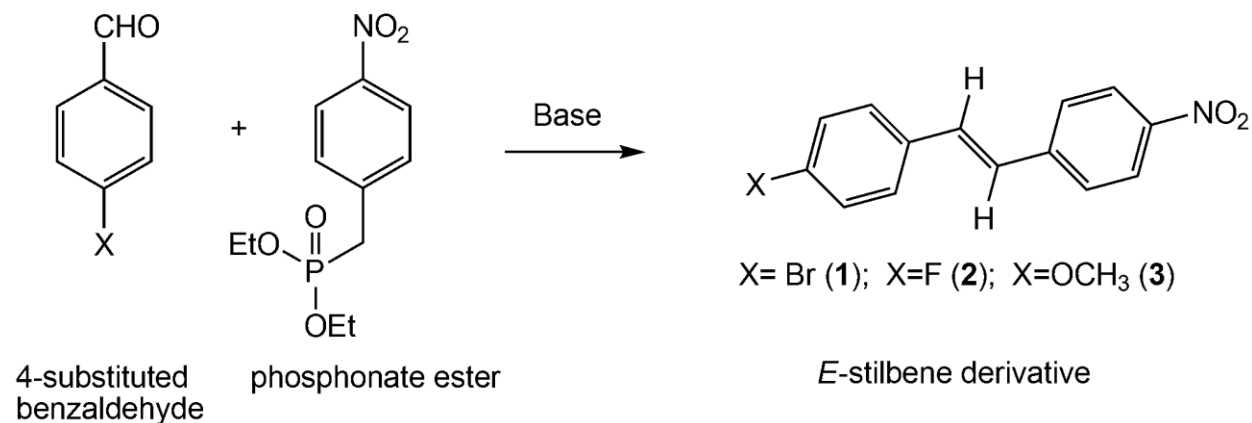


X= Br (1); X=F (2); X=OCH₃ (3)

Scheme 1 Structure of **1-3** showing the six sets of chemically equivalent protons H_a, H_b, H_c, H_d, H_e and H_f

Synthesis, colour, infrared, mass and NMR spectra

For the synthesis of compounds **1-3** the authors of the commented papers employed the well known Horner-Wadsworth-Emmons reaction protocol which involves the reaction of diethyl(4-nitrobenzyl)phosphonate with the corresponding 4-substituted benzaldehyde in the presence of a strong base (Scheme 2). This same methodology was used by Wang *et al* [6] for synthesis of several stilbene derivatives. It is to be noted that the scheme of synthesis given in all three papers [2-4] is incorrect because the same wrong structure for the diethyl(4-nitrobenzyl)phosphonate ester first shown in [4] was carried over to the later two papers.



Scheme 2. Reaction scheme for synthesis of (*E*)-4-substituted-4'-nitrostilbenes

Crystals of 4-bromo-4'-nitrostilbene **1** and 4-fluoro-4'-nitrostilbene **2** were described as yellow colored solids by Clement *et al* [9]. A commercial sample (Sigma-Aldrich) of **1** is a white to yellow solid [17] unlike the green colored crystals of **1** grown by the authors of [2]. It is even more unusual to note that a green colored compound can be transparent in the entire visible region without showing any absorption as claimed by the authors [2]. The dubious nature of crystals of **1** grown by the authors can also be evidenced from the strange TG thermogram which exhibits an impossible weight loss of more than 200 %. Under the title Material synthesis for compound **2** the authors write that '... the green coloured FONS ...' in [3] indicating compound **2** is a green solid. However, figure showing the grown crystals of **2**, displays yellow crystals. It is not clear if the pictures of grown crystals of **1** and **2** in Ref. [2] and [3] were interchanged. For compound **3** the colour of crystals in the graphical abstract and the figure of the grown crystal appear quite different indicating a mixture of phases. The IR spectra of **1** and **2** exhibit a broad signal centered at $\sim 3500\text{ cm}^{-1}$ which is not to be expected, thus indicating the impure nature of **1** and **2**.

The molecular weight of compound **1** ($\text{C}_{14}\text{H}_{10}\text{BrNO}_2$) is 304.14. However the authors not only wrongly assigned a signal at $m/e = 302.9895$ as the molecular ion peak but also claimed that the mass of **1** has been confirmed by the high resolution mass spectrum [2]. The authors are unaware that the mass spectrum of bromine compounds containing a single bromine atom, exhibits two signals of nearly equal intensity, one for the M^+ ion (molecular ion peak) and the other for $(\text{M}+2)^+$ ion, in view of the nearly equal natural abundance of the ^{79}Br (50.69%) and ^{81}Br (49.31%) isotopes [18]. The mass spectrum reported by the authors for compound **2** is extremely unusual with several signals, indicating that the spectrum is abnormal. The abnormality can only be explained either due to an instrumental artifact or due to the presence of a mixture of several compounds.

The ^1H NMR data does not provide any information on the coupling constant (J_{HH} data in Hz) and the chemical shifts for the different types of protons shown in Scheme 1 are not assigned as per the normal practice. In view of this, it cannot be confirmed if the compounds **1-3** under study in [2-4] are *cis* or *trans* derivatives. The several signals in the reported NMR spectra is a clear indication of the questionable purity of the grown crystals of **1-3**.

Inconsistencies in X-ray structure characterization and SHG studies

Both single crystal and powder X-ray diffraction analyses were supposed to have been used for the characterization of **1-3**. However, the authors do not mention if the phenyl rings are disposed *cis* or *trans* to each other [2-4]. Only unit cell parameters and the space group are reported and no other structural features are described for any of the compounds. It is not clear on what basis (systematic absences) of single crystal data, the authors have assigned the space groups. One finds the assignment of space group without solving the structure and reporting Sohncke space groups $P2_12_12_1$ (for **1**) $P2_1$ (for **2**) and $P1$ (for **3**) without giving the value of Flack parameter [19] very unusual. It is well documented that such a practice of assigning space groups without structure determination more often leads to incorrect conclusions [1, 20, 21]. The importance of a detailed X-ray structure analysis has been elegantly demonstrated by Behrnd *et al* in the case of (*E*)-4-chloro-4'-nitrostilbene which exhibits orientational disorder [14].

Without taking into consideration that the SHG efficiency in the Kurtz method depends on the particle size [22] and the inaccuracy of the Kurtz method can be as high as 50% [23], the authors have performed powder SHG experiments for these 'so called' non linear optical crystals of **1-3**. The first of these measurements was reported for **3** in [4] with the reasoning that only powder SHG studies were carried out on this material in different solvents and the work of Wang *et al* [6] was cited for this purpose. It appears that the authors of [4] did not carefully read the paper titled, 'New organic non-linear optical materials of stilbene and

diphenylacetylene derivatives' by Wang *et al.* In Table 1 of this paper Wang *et al* had given a list of several stilbene derivatives which included **1-3** and their methods of synthesis and in Table 2 of the same paper, the powder SHG data of all the compounds listed in Table 1. A notable observation of Wang *et al* was that polymorphism is a very common phenomenon of the stilbene derivatives which could explain the observation of differing SHG behavior for the same compound crystallized from different solvents in their work [6]. For compound **3** it was reported by Wang *et al* that crystals of **3** grown from dioxane solution have a centrosymmetric structure and the small SHG signal observed from the powder sample of **3** was attributed to minor amounts of other active phases. This can explain the inclusion of compounds **1** and **2** in the patent and not **3** [9].

In view of the dubious nature of crystals of **3** grown in the commented paper [4] as already discussed, the observed SHG signal can be easily attributed to the presence of a mixture of phases. In view of the questionable purity of **1** and **2** and also no information on particle size used for powder SHG study, the SHG results of these compounds can be conveniently dismissed as trash. In this context, we are quite disappointed to write that the authors of [2,3] who were aware of the reported work of Wang *et al* on compounds **1** and **2** did not cite this paper [6] but more unfortunately went on to claim that these compounds are novel organic NLO crystals after using the same abbreviation BONS used by Wang *et al* for compound **1**.

Conclusions

In summary, we have shown that the 4-substituted-4'-nitrostilbenes **1-3** are known compounds whose synthesis and SHG characteristics are well documented in the literature [5-9]. In view of the dubious nature of the grown crystals of **1-3**, the commented papers do not add any new scientific information on these well known materials. The claim of the authors of [2-4] that **1-3** are novel NLO materials can only be termed as ludicrous.

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