

# Raman spectroscopy and theoretic study of hyperpolarizability effect in diiodobutenyl-*bis*-thioquinolinium triiodide at low temperature

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Various structural features, such as proton disorder or noncovalent interactions, determine the existence of switchable nonlinear optical properties under varying external conditions. Thus, for the single crystal of diiodobutenyl-*bis*-thioquinolinium triiodide with the bridge hydrogen atom, previously characterized under ambient conditions by C<sub>2</sub>/c symmetry, we have measured Raman spectra in the temperature range from 298 K down to 113 K. Variations in low-wavenumber region of Raman spectra at temperatures below 153 K have been attributed to the change of the bridge hydrogen atom position in the [NHN]<sup>+</sup> fragment, thus lowering the crystal symmetry from C<sub>2</sub>/c to Cc. Quantum chemical calculations in the solid state for noncentrosymmetric Cc structure predict high hyperpolarizability and second-order electric susceptibilities, comparable to those of modern nonlinear optical materials. This indicates the emergence of nonlinear optical properties in the low-temperature phase of the studied crystal. Copyright © 2017 John Wiley & Sons, Ltd.

**Keywords:** polyiodides; Raman spectroscopy; noncovalent interactions; proton disorder; nonlinear optical properties

## Introduction

Organic polyiodides<sup>[1]</sup> demonstrate wide variations in noncovalent interactions with iodine participation. For this reason, they can exhibit unique properties, making them applicable as components of solar cells<sup>[2]</sup>, organic semiconductors<sup>[3]</sup> and iodine sorbents.<sup>[4]</sup> Moreover, they also display a wide range of nonlinear optical properties, as some recent studies show.<sup>[5]</sup> Design of materials, capable of nonlinear optical response, is a formidable challenge due to a number of structural limitations.<sup>[6]</sup> Symmetry questions in the case of centrosymmetric and noncentrosymmetric structures lead to uncertainties in interpretation of X-ray diffraction data,<sup>[7]</sup> so it has been suggested that the second harmonic generation (SHG) can be a powerful tool for such tasks, as it can be observed only for noncentrosymmetric systems.<sup>[8]</sup> Moreover, organic materials capable of changing their nonlinear response under different external conditions attract particular interest as optical switches.<sup>[9]</sup>

Heterocyclic N,S-containing quinoline polyiodides are prominent candidates for the usage in various fields of novel material design<sup>[10–12]</sup>, due to their great structural diversity and potentialities for functionalization. Recently, the structural features of diiodobutenyl-*bis*-thioquinolinium triiodide have been studied by X-ray diffraction and first-principles calculations.<sup>[13]</sup> The key problem of the previous research was the determination of the position of bridge hydrogen atom, resulting in uncertainty of total symmetry: C<sub>2</sub>/c [NHN]<sup>+</sup> versus Cc [N–H...N]<sup>+</sup>.<sup>[13]</sup> Recent study<sup>[14]</sup> has drawn attention to the role of polar distortions in similar hydrogen-bonded frameworks and its role in determination of ferroelectric properties. In this work, we focus on the dynamics of the bridge hydrogen atom as a function of temperature using the powerful Raman spectroscopy technique. We also investigate the influence of hydrogen localization on nonlinear optical properties by means of quantum chemical calculations.

## Experimental and computational details

Ruby-red single crystals of diiodobutenyl-*bis*-thioquinolinium triiodide (**1**) were obtained according to experimental procedure described previously.<sup>[13]</sup>

Raman spectra were measured by a confocal Raman microscope Alpha 300AR. Excitation of Raman scattering was performed by the solid state laser with wavelength 488 nm and maximum power 27 mW. Scattered light was collected by 10× objective (NA = 0.2) in backscattering geometry. The diffraction grating with 1800 lines per mm provided the spectral resolution of about 1.22 cm<sup>-1</sup>. The sample was placed into the thermal stage Linkam THMS600 cooled by liquid nitrogen and mounted onto a sample holder of the microscope. Raman spectra were measured in temperature range from 298 K down to 113 K with cooling rate 2 K/min.

First-principles density functional theory calculations at B3LYP/DZVP<sup>[15,16]</sup> level were performed using CRYSTAL14 package.<sup>[17]</sup> Vibrational frequencies for Cc (Fig. 1) and C<sub>2</sub>/c space groups were computed *via* the coupled perturbed Kohn–Sham approach at the  $\Gamma$  point of the Brillouin zone in harmonic

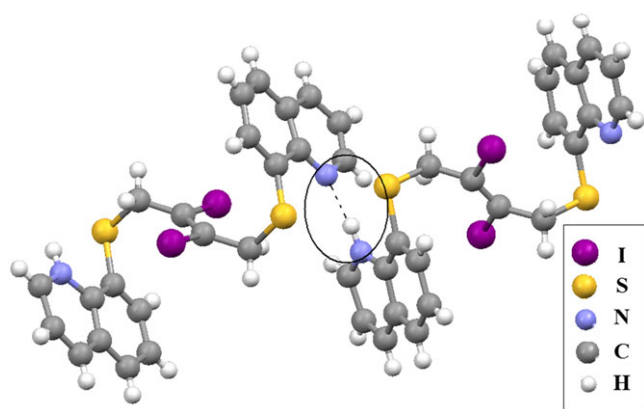
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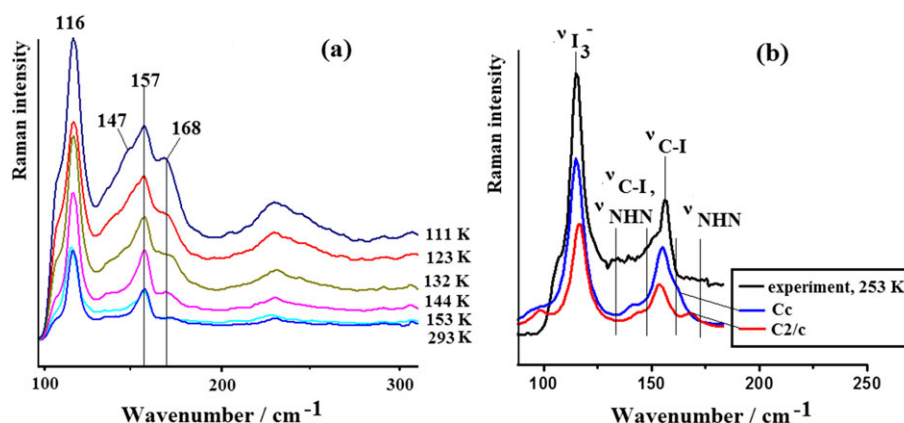
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**Figure 1.** Pair of two neighboring organic cations, forming noncentrosymmetric N—H...N fragment in Cc crystal symmetry. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

approximation.<sup>[18]</sup> The calculated Raman spectra were visualized in the pseudo-Voigt functional form. This level of calculations was previously validated by comparison with experimental Raman data for tricyclic quinolinium polyiodides.<sup>[19]</sup>



**Figure 2.** (a) Temperature dependence of experimental Raman spectra in the range from 293 to 111 K; (b) Comparison of experimental and calculated low-frequency Raman spectra for crystals with Cc and C2/c symmetry. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

**Table 1.** The calculated nonzero elements of the following tensors: polarizability  $\alpha$ , hyperpolarizability  $\beta$ , dielectric susceptibility  $\epsilon$ ; first, second and third-order electric susceptibility  $\chi^1$ ,  $\chi^2$  and  $\chi^3$  (a.u.)

Tensor element	Value, a.u.	Tensor element	Value, a.u.	Tensor element	Value, a.u.	Tensor element	Value, a.u.
$\alpha_{xx}$	1515.4	$\beta_{xxx}$	640.2	$\gamma_{xxxx}$	4282353.0	$\chi_{xxxx}^3$	971.0
$\alpha_{xz}$	416.7	$\beta_{xxz}$	320.0	$\gamma_{xxxz}$	1583053.1	$\chi_{xxxz}^3$	359.0
$\alpha_{yy}$	1513.0	$\beta_{xyy}$	-167.9	$\gamma_{xyyy}$	780439.9	$\chi_{xyyy}^3$	177.0
$\alpha_{zz}$	1779.6	$\beta_{xzz}$	2243.5	$\gamma_{xxzz}$	2887315.6	$\chi_{xxzz}^3$	654.7
$\chi_{xx}^1$	2.062	$\beta_{yyz}$	157.0	$\gamma_{xyyz}$	-165661.0	$\chi_{xyyz}^3$	-37.6
$\chi_{xz}^1$	0.567	$\beta_{zzz}$	6863.5	$\gamma_{xzzz}$	4046473.5	$\chi_{xzzz}^3$	917.5
$\chi_{yy}^1$	2.059	$\chi_{xxx}^2$	0.436	$\gamma_{yyyy}$	5781079.8	$\chi_{yyyy}^3$	1310.9
$\chi_{zz}^1$	2.421	$\chi_{xxz}^2$	0.218	$\gamma_{yyzz}$	2787390.3	$\chi_{yyzz}^3$	632.0
$\epsilon_{xx}$	3.0618	$\chi_{xyy}^2$	-0.114	$\gamma_{zzzz}$	2764465.5	$\chi_{zzzz}^3$	2894.3
$\epsilon_{xz}$	0.5670	$\chi_{xzz}^2$	1.526	$a_{\text{tot}}^b$	7826.5	BG, C2/c	3.09 eV
$\epsilon_{yy}$	3.0585	$\chi_{yyz}^2$	0.107	$a_{\text{iso}}^b$	1602.7	BG, Cc	3.01 eV
$\epsilon_{zz}$	3.4211	$\chi_{zzz}^2$	4.669	$c\Delta\alpha$	187.7	—	—

<sup>a</sup>The average hyperpolarizability  $\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)$ , where  $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$ ;  $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$ ;  $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$ .

<sup>b</sup>Isotropic polarizability  $\alpha_{\text{iso}} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ .

<sup>c</sup>Anisotropy of polarizability  $\Delta\alpha = 1/2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2]^{1/2}$ .

## Results and discussion

According to X-ray diffraction data,<sup>[13]</sup> there are no significant changes in atomic positions of the C, N, S, I atoms at room temperature and at 100 K. Nevertheless, Raman spectra demonstrate several changes in the temperature range from 153 K down to 113 K (Fig. 2a). The spectral region below 200  $\text{cm}^{-1}$  contains both the bands corresponding to the vibrations of triiodide-anion<sup>[20]</sup> (intense band at 116  $\text{cm}^{-1}$ ; location does not change under cooling) and also vibrations of NHN hydrogen bonds. At temperatures below 144 K, the band at 157  $\text{cm}^{-1}$  that was previously attributed to C—I...I<sub>3</sub><sup>-</sup> vibrations<sup>[13]</sup> widens simultaneously with the appearance of the peak at 168  $\text{cm}^{-1}$ . Further cooling down to 113 K gives rise to the band at 147  $\text{cm}^{-1}$  that is the shoulder of the initial band at 157  $\text{cm}^{-1}$ .

We have also predicted the Raman spectra in C2/c and Cc space groups (Fig. 2b). According to the literature data and theoretic simulation of Raman spectra in both space groups, these new bands can be interpreted as the vibrations of NHN fragment (Fig. 2b). These bands are close to the reported location of NHN and OHO bands for pyrazinamide (178  $\text{cm}^{-1}$ )<sup>[21]</sup> and benzoic acid (146  $\text{cm}^{-1}$ )<sup>[22]</sup>, which is in consistency with experimental and

theoretic data for compound **1** in the C2/c space group. Preliminary experiments concerning the possibility of SHG have been performed using the laser with 785-nm wavelength. No significant SHG signal has been registered under ambient conditions, as it should be in the case of centrosymmetric N...H...N fragment. Nevertheless, the possible symmetry break in the N...H...N fragment under cooling might lead to the appearance of nonlinear optical properties in the studied crystal. From the theoretical point of view, the prediction of these properties is based on nonzero elements of hyperpolarizability tensor  $\beta$  and second-order electric susceptibilities  $\chi^2$  (Table 1).<sup>[23]</sup> Because compound **1** belongs to monoclinic crystal syngony, four nonzero  $\alpha$  elements and six nonzero  $\beta$  and  $\chi^2$  elements are expected for the crystal class C<sub>1h</sub> with the mirror plane perpendicular to **y** axis.<sup>[24]</sup> Calculated values of  $\beta$  and  $\chi^2$  are comparable with organic nonlinear optical materials, such as naphthalene and azanaphthalene<sup>[25]</sup>, 2,6-dichloro-4-nitroaniline<sup>[26]</sup> and others.<sup>[27,28]</sup> The band gap values (BG) for the optimized structures in both space groups are at the level of wide band gap semiconductors (2 to 4 eV).<sup>[29]</sup>

## Conclusions

A joint consideration of low-temperature Raman spectra and first-principle calculations has allowed us to reveal the changes in proton ordering in diiodobutenyl-*bis*-thioquinolinium triiodide. Rise of the bands at 147 cm<sup>-1</sup> and 168 cm<sup>-1</sup> under cooling below 153 K indicates the changes in the NHN vibration region according to theoretic data. Possible symmetry break in the [NHN]<sup>+</sup> structure fragment should result in the appearance of nonlinear optical properties and open possibilities to use diiodobutenyl-*bis*-thioquinolinium triiodide and similar structures with oriented hydrogen-bonded networks as optical switches. Oncoming studies of the influence of various experimental conditions on existence/absence and intensity of the second harmonic generation signal is the question of further consideration.

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