

Is “nitramino sulphonic acid” really a new nonlinear optical material?

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Abstract

We prove that a so-called “nitramino sulphonic acid” crystal reported by S. Yesuvadian et al, (Optik 126 (2015) 95-100) is not a new nonlinear optical material but instead the well-known centrosymmetric sulphamic acid crystal.

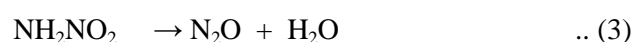
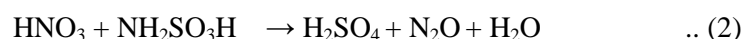
Keywords: nitramino sulphonic acid; sulphamic acid; centrosymmetric; improper characterization.

Comment

The authors of a recent paper [1] report on the growth and characterization of a so called “nitramino sulphonic acid” crystal as nonlinear optical material. According to [1] the “nitramino sulphonic acid” (hereafter **I**) is formed from aqueous solution containing equimolar quantities of nitric acid and sulphamic acid as in equation (1).



However, the reaction of nitric acid with sulphamic acid has been investigated since the 19th century (see [2-4] and references therein). It is well established that nitrous oxide N₂O (not compound (**I**)) and sulfuric acid are the actual products of this reaction (equation 2) [5], while N₂O is formed by the decomposition of nitramide (NH₂NO₂), according to equation (3).



Hughes and Lusty reported that nitramide may be isolated when the reaction (1) is performed at -50°C implying that it may be an intermediate [2]. Different schemes have been proposed for formation of

1 nitramide including one containing the compound (I) as an intermediate [2-4]. However, all attempts
2 to identify intermediates by spectroscopy and by chemical tests were unsuccessful [3].
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5 Mentioning the work of Hughes and Lusty [2] (not Martin et al. as cited in [1]) the authors of [1]
6 assumed that the compound (I) may be obtained by heating the mixture up to 79°C and then by
7 cooling to ambient temperature. White coloured substance was used for crystal growth from aqueous
8 solution at 30°C by slow evaporation. The authors of [1] have not determined the crystal structure of
9 obtained crystal and did not compare characterization results with that of starting sulphamic acid (see
10 [6]). Instead they tried to interpret data of proton NMR and high quality infrared spectra assuming that
11 the obtained material is the desired crystal namely (I). These interpretations are inconsistent and
12 erroneous. For example, the peak at 1068 cm⁻¹ in the IR spectrum the authors assigned to stretching
13 mode of SO₃ group and at the same time to rocking mode of NH₃⁺ group. Similarly, the peaks at 1450
14 cm⁻¹ and 530 cm⁻¹ are assigned to deformation of NH₃⁺ and SO₃⁻. However, no NH₃⁺ group is present
15 in the supposed molecule of (I): O₂N-NH-SO₃H. The peak at 1002 cm⁻¹ was assigned to stretching
16 vibration of O-H hydrogen bond. Such low frequency position of ν(OH) presumes the presence of
17 very strong hydrogen bond and knowing the crystal structure. Actually the IR spectrum reported in [1]
18 perfectly coincides with the spectrum of sulphamic acid (see e.g. [7], where detailed assignment of
19 peaks was performed). This means that a so called “nitramino sulphonic acid” crystal is actually
20 sulphamic acid. Further, the formation of sulphamic acid crystal clearly indicates that the crystal
21 growth reaction was not performed using equimolar ratios but by use of a large excess of sulphamic
22 acid reagent which was actually recovered. As it is well known that the zwitterionic sulphamic acid is
23 soluble in water and insoluble in organic solvents like CHCl₃, one really wonders as to how authors
24 recorded the proton NMR spectrum of such a compound in CDCl₃.
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51 The crystal structure of sulphamic (sulfamic, or aminosulfonic) acid existing as the zwitterionic
52 (H₃N)⁺(SO₃)⁻ species, was first reported in the centrosymmetric orthorhombic *Pbca* space group with
53 cell parameters: *a*=8.066(1) Å, *b*=8.115(1) Å, *c*=9.255(3) Å [8]. Later its symmetry was confirmed
54 and crystal structure was refined [9-11].
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The authors of [1] provided powder X-ray diffraction pattern of (I) and measured cell parameters: $a=8.0617 \text{ \AA}$, $b=8.1116 \text{ \AA}$, $c=9.2310 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$. As one might expect cell parameters of (I) are in good agreement with that measured in [8] for sulphamic acid. Accordingly powder X-ray diffraction pattern of (I) coincides with that of sulphamic acid which has been published numerous times. The authors of [1] indicated for (I) noncentrosymmetric space group $Pba2$, which without structure determination cannot be considered as trustworthy.

The claim of observation of a second harmonic generation signal in (I) [1] which is actually centrosymmetric sulphamic acid, also appears unreliable. This confusion has a prehistory and was first started by the authors of [12]. In spite of the fact that the authors of [13] pointed out that sulphamic acid cannot display SHG because of centrosymmetric structure and actually does not display any second harmonic signal, papers describing “NLO properties of sulphamic acid” have unfortunately been published [14-16]. Interestingly, the authors of [16] in their introduction write about “*outstanding piezoelectric and non-linear optical (NLO) properties*” and quoted the paper of E. Haussühl and S. Haussühl [17] which actually reported on the elastic and thermoelastic properties of sulphamic acid crystal and not piezoelectric and nonlinear optical properties. Similarly the authors of [1] cited the paper [13] for SHG active crystals, where it is actually mentioned that sulphamic acid is not SHG active. We leave all claims of observations of second harmonic generation in centrosymmetric crystal of sulphamic acid to the conscience of these authors.

In summary, we have proved that a so called “nitramino sulphonic acid” crystal reported by S. Yesuvadian et al [1] is neither a new crystal nor a nonlinear optical material because it is actually the well-known centrosymmetric sulphamic acid crystal.

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