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Comments on "A comprehensive experimental and computational study of highly efficient organic NLO crystal: Anilinium -L-Tartrate"

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Highlights

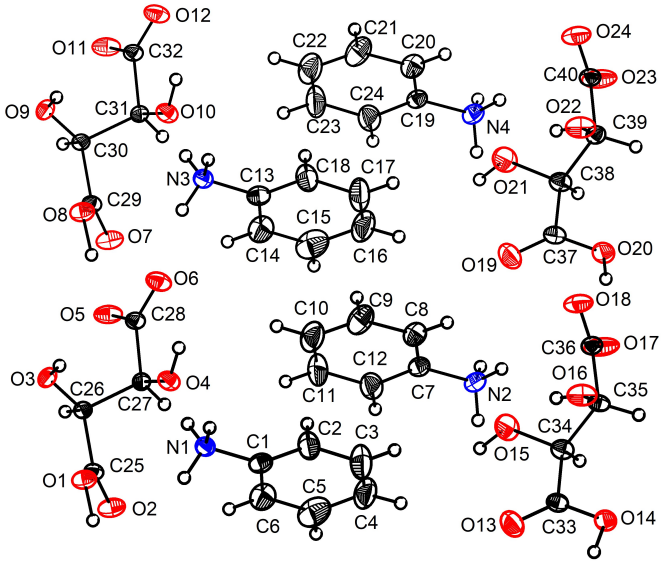
Growth of anilinium L-tartrate (ALT) crystal is critiqued

Yellow colour of ALT is due to surfacial oxidation

Structure data in the title paper contradict literature report

Graphical abstract

The room temperature structure of the 1:1 binary salt of aniline and L-tartaric acid consists of four unique anilinium cations and four crystallographically independent hydrogen tartrate anions.



Abstract

The authors of the title paper (Optics & Laser Tech **137** (2021) 106800) claim to have performed an experimental and computational study of anilinium L-tartrate (ALT) crystal. In this letter to Editor, it is shown that the ALT crystal is a surface degraded material. A critical analysis of the title paper is presented to show that the reported experimental data contradict earlier reports on the 1:1 salts of aniline and L-tartaric acid.

Keywords: *crystal growth; anilinium L-tartrate; crystal structure; surface degradation optical materials and properties;*

Dear Editor

Recently I became aware of the title paper [1] published in *Optics and Laser Technology*. A perusal of the article by Sudha et al [1] reveals that the anilinium L-tartrate (ALT) crystal has undergone surface degradation. In the following comment it will be proved that several claims in the title paper are erroneous.

The authors of the title paper report to have grown pale yellow crystals of ALT by the slow evaporation of an aqueous solution containing aniline (0.96 g) and L-tartaric acid (0.56 g). Both aniline and L-tartaric acid are colorless chemicals. Hence a product of these two reagents can be expected to be colorless. Unlike ALT, two earlier reported 1:1 salts of aniline and L-tartaric acid viz. anilinium L-tartrate and anilinium L-tartrate monohydrate (ALTM) are colorless [2,3]. It is well documented in standard organic chemistry text books [4] that aromatic amines and their compounds are prone to air oxidation. In a recent paper the extent of surface degradation of o-phenylenediammonium salts has been shown to depend on the exposure time [5]. A commercial sample of aniline is colored and hence it is a standard practice to either employ a freshly distilled sample of aniline for synthesis or recrystallize the final product as reported for the colourless ALTM crystal [3]. From the experimental details of ALT synthesis, it is noted that the amount of reagents (0.96 and 0.56 g respectively) correspond to a mole ratio of 2.76:1 of aniline:L-tartaric acid and not equimolar amounts. The excess of aniline present in the reaction medium gets slowly air oxidized and

can explain the yellow color of the ALT crystal (Fig S1 Supplementary Material) instead of the colorless crystals [2,3] reported previously.

The reaction of aniline with L-tartaric acid was first studied by Yoshii et al [2]. The crystal of anilinium L-tartrate **1** (the anion present is actually L-hydrogen tartrate) was obtained by reaction of aniline with L-tartaric acid in 1:1 ratio in ethanol-water (8:2 v/v) medium [2]. Kanagathara et al [3] have reported to have isolated a colorless anilinium L-tartrate monohydrate (ALTM) by reaction of equimolar amounts of aniline with L-tartaric acid in aqueous medium (Table S1). In contrast, the authors of the title paper claim to have obtained ALT, which is anhydrous, from an aqueous solution. The authors of the title paper are unaware of the earlier reports [2, 3] on the 1:1 salts of aniline and L-tartaric acid.

The monohydrate ALTM crystallizes in the monoclinic $P2_1$ space group (Table 1). For the room temperature (293 K) crystal structure of ALT refined in the triclinic $P1$ space group, the cell volume is reported as 545.99(3) $Å^3$ with Z=2 (Table 1) showing the presence of two unique anilinium cations and two hydrogentartrate anions. However, for the anhydrous 1:1 salt of aniline and tartaric acid, which crystallizes in the triclinic $P1$ space group, Yoshii et al [2] have reported that the room temperature (300 K) structure consists of four unique anilinium cations and four crystallographically independent hydrogentartrate anions (Fig. 1) with a cell volume of 1106.2(2) $Å^3$.

Table 1. Crystallographic data reported by Sudha et al [1], Yoshii et al [2] and Kanagathara et al [3]

Crystal	Temperature (K)	Space group	Z	*a*, *b*, *c* (in Å)	α, β, γ (in °)	Volume ($Å^3$)
ALT	293	$P1$	2	6.1496(2), 7.4156(2), 12.9784(4)	86.323(2), 76.579(2), 71.5230(10)	544.99(3)
1	300	$P1$	4	8.0322(6), 11.0953(8), 13.0247(9)	100.127(2), 96.793(2), 101.350(2)	1106.2(2)
1	100	$P1$	2	6.1165(8), 7.466(2), 12.960(2)	89.758(5), 76.883(4), 70.706(5)	543.9(2)
ALTM	295	$P2_1$	4	9.615(2), 7.316(1), 17.311(3)	90.0, 96.47(1), 90.0	1210.0(4)

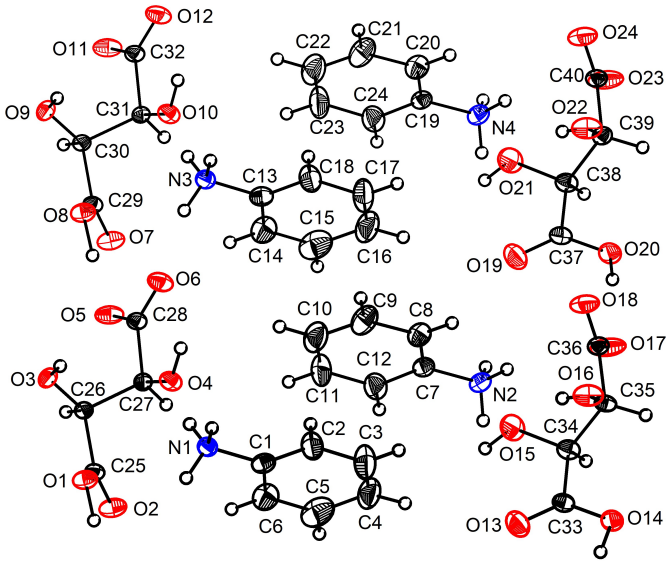


Fig. 1 The asymmetric unit of anilinium L-tartrate reported by Yoshii et al. Thermal ellipsoids are drawn at 30% probability level for all non-hydrogen atoms. Figure is drawn by using CIF file from [2]

Yoshii et al have performed a systematic structure investigation of anilinium L-tartrate at 100, 250 and 300 K respectively and have shown that the low temperature (100 K) phase exhibits a cell volume of 543.9(2) $Å^3$ with Z=2 unlike the room temperature (300 K) phase which has double the cell volume due to the thermal fluctuation of the polar –OH group in this phase. In addition, these authors have investigated the structural phase transitions induced by molecular motions in the anilinium L-tartrate crystal and have also reported on the dielectric properties. In contrast, the room temperature cell volume (545.99(3) $Å^3$) of the title crystal corresponds to the low temperature phase reported by Yoshii et al. The structure refinement with several unexplained restraints accompanied by a very high R value (for all data) of 9.8 % (wR2=20.86%) indicates that the work is unreliable. Although authors reported, "*Atomic positions are taken from the crystallographic information file (CIF) for geometry optimization*" the CIF file of the ALT crystal was not submitted to the Cambridge Structural Database (CSD) [6]. The questionable nature of the structure of ALT is revealed by the mismatch of the structure data with theoretical calculations. The experimental IR, Raman and optical spectra differ considerably from the theoretically predicted spectra due to i) the questionable data and ii) use of a surface degraded material for recording spectra. Despite the questionable results, authors end their paper stating, "*Thus the complete studies nominate ALT as an excellent material for NLO device*

fabrication". However, I am of the opinion that the title paper does not add any new findings on anilinium L-tartrate but only creates confusion in the scientific literature of anilinium salts of L-tartaric acid.

In summary, this critique proves that the yellow color of the title anilinium L-tartrate crystal is due to surface degradation and the synthetic and structure investigations of ALT are inconsistent with earlier literature reports.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

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Supplementary Material (ONLINE Version)

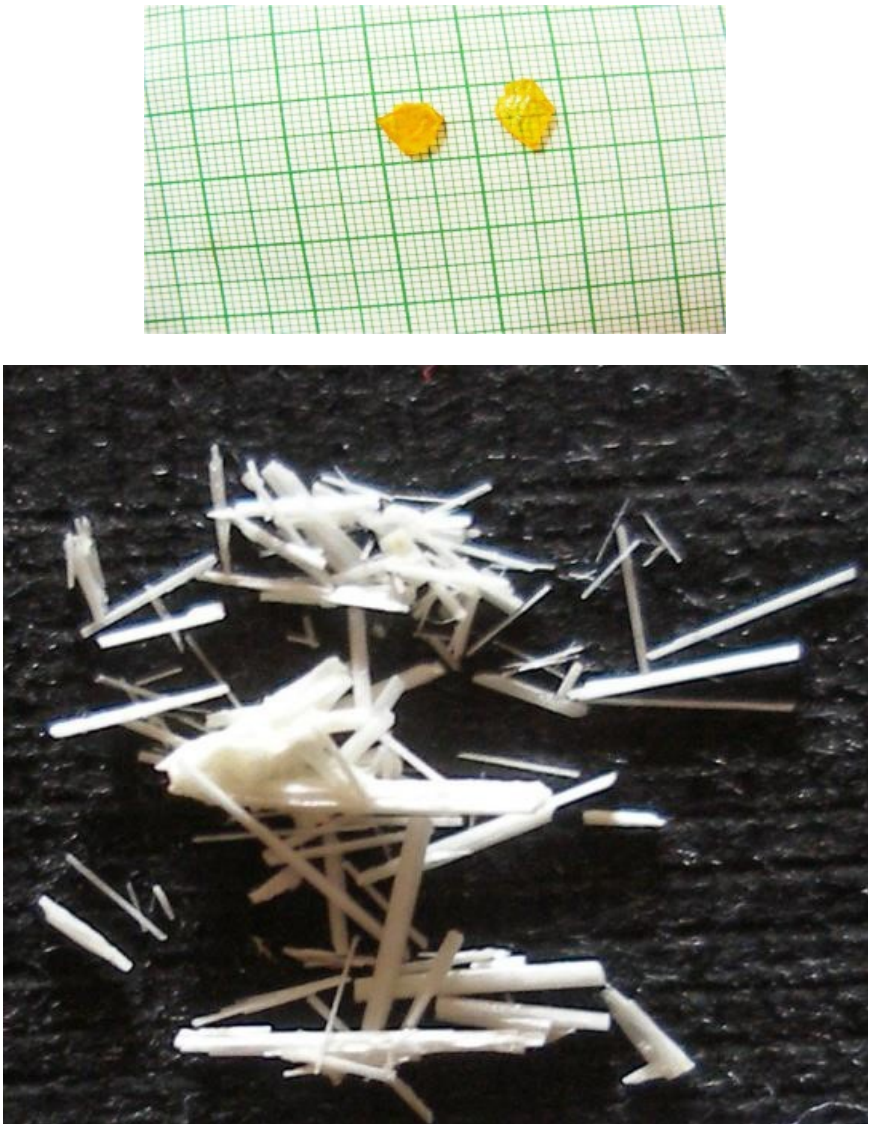

Fig S1 Yellow crystals of $(C_6H_5NH_3)(C_4H_5O_6)$ ALT (**top**) reported by Sudha et al [1]. Experimental details do not mention if both blocks were obtained in one experiment or from two different experiments. Note that the block of crystal on the left is more colored indicating more surface degradation. Crystals of $(C_6H_5NH_3)(C_4H_5O_6)\cdot H_2O$ ALTM reported in [3] (**bottom**).

Table S1 – Synthetic details of ALT and earlier work on 1:1 salts of aniline/ L-tartaric acid

Aniline ($C_6H_5NH_2$)	L-tartaric acid ($C_4H_6O_6$)	Solvent	Crystal color	Molecular Formula of product crystal	Ref
2.76 mole*	1 mole	water	Yellow	$(C_6H_5NH_3)(C_4H_5O_6)$	[1]
1 mole	1 mole	ethanol:water (8:2)	Colorless	$(C_6H_5NH_3)(C_4H_5O_6)$	[2]
1 mole	1 mole	water	Colorless	$(C_6H_5NH_3)(C_4H_5O_6)\cdot H_2O$	[3]

*Authors incorrectly reported in [1] that reaction was performed in 1:1 ratio.