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Comments on the paper: "Studies on the Third order nonlinear Optical Properties of a novel *o*-Phenylenediaminium *p*-Toluenesulfonate single crystal"

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Highlights

The title paper is critiqued

o-Phenylenediaminium *p*-toluenesulfonate **1** is a dubious crystal

Dark brown colour of **1** is due to extensive surficial oxidation

o-phenylenediaminium bis-hydrogen phosphonate **3** is a dubious crystal

Salts of *o*-phenylenediamine undergo slow air oxidation in solution

Abstract

The authors of the title paper (Materials Letters **247** (2019) 25–28) report to have grown dark brown single crystals of *o*-phenylenediaminium *p*-toluenesulfonate (PTOP) by slow evaporation of an aqueous solution containing *o*-phenylenediamine and *p*-toluenesulfonic acid. In this communication, many points of criticism, concerning the crystal growth and color of this so-called PTOP crystal are discussed to show that the dark brown color is due to extensive surficial oxidation. The brown color of *o*-phenylenediaminium bis-hydrogen phosphonate (P2HP) crystal reported by the same group (Materials Letters, **209** (2017) 167-170) is explained due to surface decay. Because of surface degradation, the grown crystals are impure and the reported optical properties are questionable.

Keywords: *Crystal growth; Crystal structure; o-phenylenediaminium p-Toluenesulfonate; o-phenylenediaminium bis-hydrogen phosphonate; dubious crystal; surface decay*

Introduction

The title paper [1] reporting the crystal growth of *o*-phenylenediaminium *p*-toluenesulfonate (called as PTOP by authors) attracted my attention due to i) the unusual name of the so-called novel compound and ii) our recent research interest in the salts of *o*-phenylenediamine [2, 3]. Since *o*-phenylenediaminium is a dication and *p*-toluenesulfonate refers to a mononegative ion, the title paper was perused to determine what such a compound can be. The scrutiny revealed several inconsistencies in the claims, which are described in the following comment. Throughout this paper, compounds are referred to by numbers to avoid the use of long names and peculiar codes like PTOP and P2HP.

Comment

*o-phenylenediaminium p-toluenesulfonate **1** is a dubious crystal*

The authors of [1] reported to have grown single crystals of **1** by slow evaporation of an aqueous solution containing *o*-phenylenediamine (1.36 g) and *p*-toluenesulfonic acid (2.3 g) in 1:2 mole ratio. Although the authors claim to have performed a 1:2 reaction, the quantities of reagents correspond to a mole ratio of 1:1.06. Recently, we reported that an aqueous reaction of *o*-phenylenediamine and *p*-toluenesulfonic acid in 1:2 ratio results in the formation of benzene-1,2-diaminium bis(4-methylbenzene-1-sulfonate) and not any **1** [2]. In their discussion of single-crystal study, authors mentioned that the grown crystal belongs to the triclinic system ($P\bar{1}$ space group) and reported only the unit cell dimensions without any esd (Table 1) and ended the discussion with the statement, "*These crystal data very well agree with the reported data '[4]'*" where the citation '*[4]*' is an IUCrData report [4] by the same group on the structure of 2-aminoanilinium benzene-1,2-diaminium tris(4-methylbenzene-1-sulfonate) **2**. It is not clear why a known crystal reported in an earlier paper [4] is referred to by a different name and termed a novel compound by the same authors. Regrettably, the name of compound **1** indicates charge imbalance and hence scientifically inappropriate.

Table 1. Crystallographic data of o-phenylenediaminium p-toluenesulfonate **1** and 2-Aminoanilinium benzene-1,2-diaminium tris(4-methylbenzene-1-sulfonate) **2**

Compound	Colour	Space group	*a*, *b*, *c* (in Å)	α, β, γ (°)	V (in Å^3)	Ref
2	Colorless	$P\bar{1}$	10.5058(4), 12.8929(4), 14.0425(4)	80.187(2), 73.218(1), 89.188(2)	1793.17 (10)	[4]
1	Dark brown	$P\bar{1}$	10.5058, 12.8929, 14.0425	80.187, 73.218, 89.188	1793.17	[1]

From the identical cell parameters (Table 1), one cannot infer if the unit cell of **1** was actually determined or the cell parameters of **2** (without esd) are reported once again. A perusal of the experimental details in [1] and [4] reveals that same quantities of reagents were employed for the growth of **1** as well as **2**. Although it is not clear if the big crystalline blocks of **1** were grown using the same amount of reagents as for **2**, it is surprising to note that crystals of **1** are dark brown (Fig S1), unlike the colorless crystals which were reported from the same reaction in an earlier paper [4] by the same authors.

Pure *o*-phenylenediamine and *p*-toluenesulfonic acid are colorless solids. Hence a product of these two reagents is expected to be colorless as reported recently for the 1:2 and 1:1 salts of *o*-phenylenediamine [2, 3] and earlier for **2** [4]. A dark brown solid is expected to absorb in the visible region. However, the authors reported in the highlight that **1** is transparent in the entire visible region but did not offer any explanation for this contradiction. It is well documented in standard organic chemistry text books [5] that aromatic amines and their compounds are prone to air oxidation. A commercial sample of *o*-phenylenediamine is colored because of surface oxidation and it is a standard practice to employ a freshly recrytallized sample of *o*-phenylenediamine in synthesis [2, 3]. Hence, the brown color of **1** is due to the surficial oxidation due to long aerial exposure, as evidenced from the forty-eight days time taken for crystal growth of **1**, instead of a week for the crystals of **2**. In view of the surface degradation, which has not been considered by the authors, the spectral data and studies of optical properties are meaningless and claims such as '*the grown crystal is suitable for optical devices'* can be summarily dismissed.

From the space group it can be inferred that **1** is a centrosymmetric solid. Hence referring to **1** as an organic nonlinear optical (NLO) material in the abstract and an elaborate description of NLO materials in the introduction is inappropriate.

*o-Phenylenediaminium bis-hydrogen phosphonate **3** [6] is a dubious crystal*

The crystal growth of a phosphorous acid salt of *o*-phenylenediamine (compound **3**) was reported by the same group who described the growth of surface degraded crystals of **1**. Although the title of the paper indicates **3** is a novel organic material, the structure of **3**, which crystallizes in the centrosymmetric monoclinic C2/c space group was already reported by the same authors in an IUCrData report [7] under a different name viz. benzene-1,2-diaminium bis-(hydrogen phosphonate) **4**. The reason for changing the name of a known crystal **4** in their later publication [6] is not clear. In this context, it should be noted that writing more papers on the same compound with different names creates confusion in the scientific literature and hence is not a desirable activity. The salt **4** obtained by reaction of phosphorous acid with *o*-phenylenediamine is colorless, as evidenced from the CIF file of compound **4**, which is archived in the Cambridge Structural Database (CSD) [8]. However, a crystalline block of **3** [6] grown by the slow evaporation method over twenty days is brown with some white patches (Fig S2). The color of **3** confirms the surface degradation of the organic diaminium salt and its lighter shade as compared to the dark brown color of **1** is due to less exposure to atmospheric oxygen because of the lesser duration of crystal growth.

In the discussion of laser damage threshold value of **3** the authors of [6] reported, '*The comparison for laser damage threshold and NLO parameters with well-known materials is listed in the Table 1*'. Since the first entry in this list is KDP, which is a noncentrosymmetric solid, its comparison with **3** is inappropriate. In the Table all the so called '*well-known*' materials are identified by weird codes without any explanation of the abbreviation. Due to surface decay, the optical properties and other studies of **3** are devoid of any scientific merit and hence are not discussed any further.

Conclusions:

A critical analysis of the crystal growth reactions of o-phenylenediammonium salts reported in [1, 6] reveals that the crystals described in the title paper and [6] are not novel materials but known crystals with changed names. The dark brown or the lighter shades reveal that the surfaces of the bulk crystals are oxidised. The extent of surface degradation of is dependent on the exposure time. Bulk crystals of these materials can be grown in pure form in an oxygen free atmosphere.

Acknowledgments

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Declaration of conflict of interest: None

Footnotes

[1] compounds are referred to by numbers to avoid long names and peculiar codes
[2] compounds **2** and **1** are same despite different names
[3] compounds **4** and **3** are same despite different names

References

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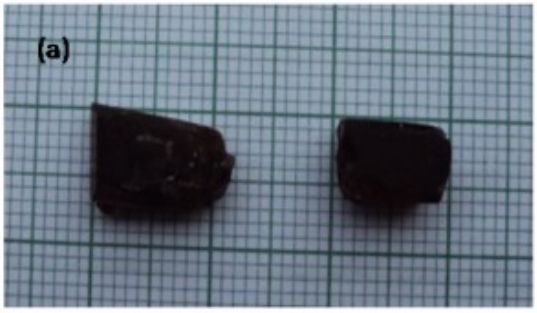
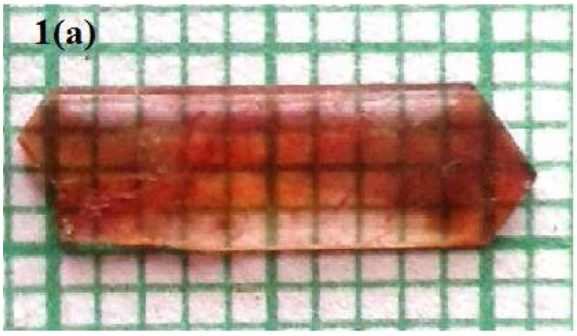
SUPPLEMENTARY MATERIAL for ONLINE VERSION

Below is Fig S1. Reproduced with permission from [1]



The legend for the above figure in [1] is as follows: **Fig. 1 (a)** Photograph of as grown PTOP crystal
Note: Duration of crystal growth 48 days

Below is Fig S2. Reproduced with permission from [6]



The legend for the above figure in [6] is as follows: Fig.1(a) Photograph of as grown P2HP crystal
Note: Duration of crystal growth 20 days

A so called P2HP crystal (compound **3**) is brown (**Fig S2**) with white patches due to less surface decay unlike the so called PTOP crystal (compound **1**) which is dark brown (almost black). This difference in color is due to extensive surface degradation of the PTOP crystal.