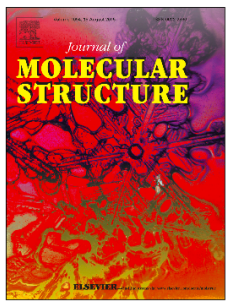

Comments on the paper 'Co-crystals of urea and hexanedioic acid with third-order nonlinear properties: An experimental and theoretical enquiry'

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S.G. Naik : Crystal growth studies

Comments on the paper 'Co-crystals of urea and hexanedioic acid with third-order nonlinear properties: An experimental and theoretical enquiry'

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Abstract

The authors of a recent paper (*J. Mol Struc.* **1202** (2020) 127237) claim to have grown a so-called 'urea hexanedioic acid' (UHA) cocrystal by the slow evaporation of an aqueous solution containing equimolar amounts of urea and hexanedioic acid. In this comment, many points of criticism, concerning the crystal growth, single crystal data, IR spectrum and theoretical study of the so called UHA crystal are highlighted to prove that the title paper is completely erroneous.

Keywords: *Urea; hexanedioic acid; urea hexanedioic acid; urea-adipic acid; dubious crystal*

Introduction

The purpose of the present comment is to show that the claims made by Jeeva et al [1] on a so called 'urea hexanedioic acid' cocrystal are untenable and thus prove that the title paper is completely erroneous. The chemistry of urea and its compounds is a well studied area of research since its first laboratory synthesis was reported by Wöhler in 1828 [2]. With acids urea is known to form cocrystals (molecular adducts) and a very early study on this aspect was reported by Dalman in 1934 [3]. A wide range of structurally characterized urea-dicarboxylic acid cocrystals are well documented in the literature [4-12]. In all these compounds, the organic acids form stable hydrogen-bonded systems with urea. In view of varying stoichiometries, it is customary to refer to the urea based compounds as 2:1 or 1:1 as the case may be.

Although urea crystallizes in the non-centrosymmetric tetragonal space group $P\bar{4}2_1m$ [13], it is known to form several molecular adducts in 2:1 and / or 1:1 molar ratios with α,ω-alkanedicarboxylic

acids many of which crystallize in centrosymmetric space groups. For some acids, particularly for oxalic, succinic and glutaric acids [5-11], crystals with both ratios are known; for adipic acid (also known as hexanedioic acid) only a 2:1 urea-adipic acid (2/1) cocrystal is known till date [12]. A claim of growth of a 1:1 urea-adipic acid crystal reporting only the unit cell parameters in the single crystal study by Shanthi et al [14] has appeared in the literature. However, questions pertaining to the unit cell and the infrared spectral data were raised showing that this work is unreliable [15].

Disregarding the centrosymmetric nature of urea-dicarboxylic acid cocrystals, several claims have appeared in the literature reporting discovery of SHG properties which were proved to be erroneous. Claims of ferroelectric properties for "urea oxalic acid" cocrystals have been proved to be erroneous [16]. Several urea based crystals have been shown to be dubious materials [17-22]. Recently we have confirmed that a so called urea oxalic acid (also reported by Jeeva et al) is not parabanic acid but is in fact the well-known 2:1 adduct namely bis-urea oxalic acid [23]. Hence the paper by Jeeva et al [1] reporting on a so called 'urea hexanedioic acid' (UHA) cocrystal abbreviated by the code UHA instead of a molecular formula but referred to as urea-adipic acid in the abstract attracted our attention. A perusal of the title paper with an incorrect formula for urea in the introduction, revealed several inconsistencies which are discussed in the following comment.

Comments

The authors of the title paper claim to have grown a so called 'urea hexanedioic acid' by slow evaporation of an aqueous solution containing equimolar amounts of urea and hexanedioic acid (adipic acid) in 1:1 ratio. Instead of reporting the quantities of reagents employed for crystal growth and the yield obtained, the authors presented the molecular structure of UHA while discussing the synthesis. It is not clear if the proposed structure is a result of the single crystal study or if it is an optimized structure from the computational study. Although the structure indicates that UHA is a 1:1 adduct of urea and hexanedioic acid, it is inconsistent with infrared spectral assignments of the authors for C=C, COO^-, NH_3, $-CH_3$ and N-O vibrations. Unfortunately, the authors did not take into

consideration that none of these fragments are present in their proposed molecular structure of UHA or are constituents of either urea or hexanedioic acid.

In the discussion of the single crystal structure where no molecular formula or details of CIF file are given the authors of the title paper mentioned, '*The compound crystallizes in the crystal form with a space group of P and monoclinic system. The attained lattice parameters are summarized in Table 1. The parameters of the unit cell coincide with the reported work [13]. Table 2 represents the geometry parameters of the molecules obtained by XRD and by theoretical calculations. It is evident from the table that the experimental and theoretical values aggress within the stipulated limits [16]*' where the citations *[13]* and *[16]* are presently [14] and [12] respectively. A perusal of [14] by Shanthi et al reveals that this work is on a so-called urea adipic acid (UAA) crystal. It is not clear why the authors of the title paper have used a different name 'urea hexanedioic acid' and code (UHA) despite the claim that the unit cell of UHA coincides with that of UAA (Table 1). Although the authors of [14] mentioned, '*The structure was solved by direct method and refind by the full matrix least squre fit technique employing the SHELXL programme*' they did not report any structure or a CIF file to substantiate the same but only a molecular formula ($CH_4N_2O{\cdot}C_6H_{10}O_4$) which indicates that UAA is a 1:1 adduct of area and adipic acid. The dubious nature of this claim on UAA can be evidenced from the assignments of NH_3^+ asymmetric stretching, CH_3 symmetric deformation (isopropyl), NO_2 rocking, N-O stretching, C=C, COO^-, N…O, vibrations in the IR spectral discussion. Although the basis of such assignments is not very clear, it is noted that such moieties are not present either in urea or adipic acid.

Table 1. Crystallographic data of urea adipic acid (2/1), so called UAA, so called UHA

Compound name	Space group	*a*, *b*, *c* (in Å)	α, β, γ (°)	Volume (Å)^3	Ref
Urea-adipic acid (2/1) $2(CH_4N_2O){\cdot}C_6H_{10}O_4$	*P-1 Z=2*	7.2484(14), 7.6965(15) 11.964(2)	101.81(3), 92.55(3), 91.92(3)	652.0(2)	[12]
Urea adipic acid (UAA) $CH_4N_2O{\cdot}C_6H_{10}O_4$	*$P2_1/c$** *Z=2*	8.303(10), 7.231(2) 10.996(7)	90, 97.5, 90	655.25(9)	[14]
Urea hexanedioic acid (UHA)#	*$P2_1/c$**	8.36, 7.31, 11.07	90, 97.03, 90	671	[1]

*No CIF file reported; #No molecular formula

According to Jeeva et al [1] the experimental geometric parameters of UHA are taken from *[13]* for a comparison of the results of their theoretical study. Unfortunately *[13]* which is the questionable claim of Shanthi et al [14] did not report any bond lengths or bond angles and so also the title paper. Hence it is not clear how (and from where) the authors got the experimental data. In the abstract the authors claim "*The structural properties of the UHA crystal were computed utilizing the CAM-B3LYP method and 6e311þþG(d,p) basis set and found agreeable with the experiment data (XRD)*". However, the experimental data in the title paper and the earlier work [14] are only limited to reporting unit cell parameters. Hence, the single crystal study reported in both these papers on so-called UAA and UHA can be dismissed as dubious due to the absence of accompanying CIF file. Although it is not clear what the authors mean by '*It is evident from the table that the experimental and theoretical values aggress within the stipulated limits [16]*' it is to be noted that *[16]* is presently [12] and is a structure report on urea-adipic acid (2/1) crystal by Chang and Lin. The structure of urea-adipic acid (2/1) reported in [12] consists of two unique urea molecules hydrogen bonded to two crystallographically independent adipic acid molecules located in special position (Fig. 1) unlike the proposed molecular structure of UHA which indicates that all atoms of both urea and adipic acid are located in general position. In view of missing details like the coordinates of the atoms in the crystal structure employed for optimization, non availability of any CIF file in the Cambridge Structural Database [24] for any so called UHA or UAA and questionable experimental bond distances and bond angles, the results of the computational study cannot be considered as reliable scientific findings.

From the above discussions it is obvious that of the three urea based cocrystals listed in Table 1 only the work of Cheng and Lin [12] on the 2:1 adduct of urea-adipic acid (2/1) is reliable and the other two papers of Jeeva et al [1] and Shanthi et al [14] on so called UHA or UAA are highly questionable despite the fact i) that these papers are published in leading peer reviewed international journals and ii) the unit cells of UHA and UAA are same but are different from that of urea-adipic acid (2/1). Interestingly the solvent employed for crystal growth was methanol and water respectively for UAA and UHA, while for the growth of 2:1 (bis urea) adduct, water was used as solvent by Chang and Lin [12]. With a view to determine the exact nature of the grown crystals of UHA and UAA, we have

performed some crystal growth experiments in aqueous and methanolic media. We have thoroughly scrutinised the published paper of Jeeva et al [1] and also the work of Shanthi et al [14] by performing crystal growth reactions both in methanol and water by using 2:1 and 1:1 mole ratios of urea:adipic acid (hexanedioic acid). In our experiments only a bis(urea)-adipic acid adduct viz. 2:1 product was obtained as the product. Use of more than 2 moles of urea in methanol or water afforded the 2:1 adduct readily. When a 1:1 reaction is performed in water the initial product obtained is adipic acid. Removal of adipic acid crystals from the reaction medium, results in enhancement of ratio of urea. After this the 2:1 product is obtained.

It is to be noted that unlike for other dicarboxylic acids, a detailed study of the phase diagram of the urea / adipic acid / water system has not been done so far, to infer if an incongruent 1:1 adduct and other products exist. While a 1:1 adduct of urea-adipic acid may exist, such a crystal cannot be obtained by use of equimolar ratios of urea and adipic acid (or hexanedioic acid) as claimed by Jeeva et al [1] and Shanthi et al [14] as proved by our above discussed experiments. No new crystal other than the well-known bis(urea)-adipic acid reported by Cheng and Lin can be obtained by changing the reactant ratio to 1:1.

Conclusions

In summary we have shown that the single crystal data and theoretical studies reported in the title paper are highly questionable and the so called crystals of urea hexanedioic acid (UHA) and the previously reported urea adipic acid (UAA) crystals are dubious materials. We sincerely hope that based on our critical comments on the results of the published papers on urea adipic acid [14] or urea hexanedioic acid [1] these or other authors will be able to obtain under appropriate conditions, a genuine 1:1 adduct of urea hexanedioic acid if such a crystal really exists.

Declaration of competing interest

None

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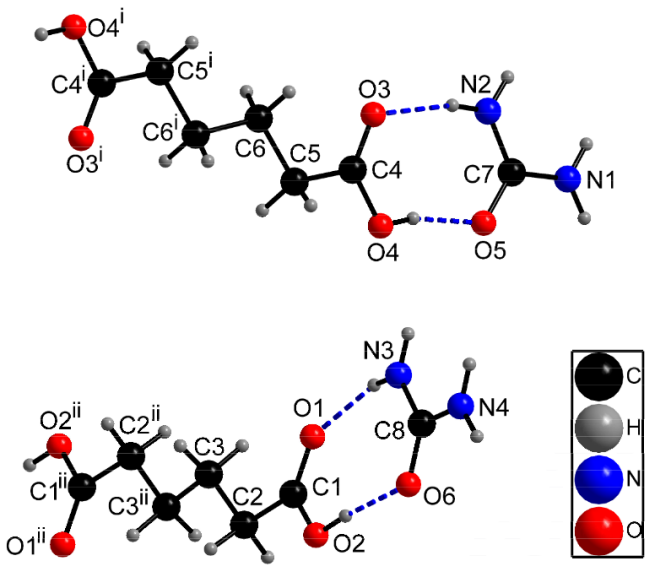

Fig. 1 Crystal structure of urea-adipic acid (2/1) showing the intramolecular H-bonding in broken lines. Symmetry code: i) –x, -y, 1-z ii) 2-x, 1-y, 2-z. Figure drawn using the reported CIF file in [12]

Comments on the paper 'Co-crystals of urea and hexanedioic acid with third-order nonlinear properties: An experimental and theoretical enquiry'

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Highlights

- The title paper is critiqued
- Many points of criticisms are highlighted
- Experimental data reported in the title paper are discussed
- Urea hexanedioic acid is a dubious crystal