described for Form E, resulting in a two-phase system: the neutral free base (common to both decomposition processes) and, in the present case, a novel Zolpidem tartrate monohydrate, unique to the "aging driven" decomposition. Our R.T. single crystal analysis gives for the free base comparable results as the H.T. XRPD ones already reported: orthorhombic, Pcba, a= 9.6360 (10)Å, b= 18.2690 (5)Å, c= 18.4980 (11)Å, V= 3256.4 (4)Å^3. The unreported Zolpiden tartrate monohydrate, instead, crystallizes in monoclinic $P2_1$, which for comparison purposes we treated in the non-standard setting $P112_1$ with a= 20.7582 (9)Å, b=15.2331 (5)Å; c= 7.2420 (2)Å, γ= 90.826 (2)°, V= 2289.73 (14) Å^3. The structure presents two complete moieties in the asymmetric unit (z=4, z'=2). The different phases obtained in both decompositions are readily explained considering the diverse genesis of both processes.

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Exploring phases of a physiologically-active nitronyl nitroxide free radical

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Nitronyl nitroxides are free radicals that are interesting both in biology and magnetism [1], [2], [3]. Their crystal structures have been largely studied: over 300 are reported. The study of different phases (polymorphs, salts, co-crystals) is relevant because properties strongly depend on crystal structure; therefore, about 13% of the structures quoted above are polymorph. In one remarkable case, 10 polymorphs have been found for a single compound [4].

Derivatives of 2-phenyl-4,4,5,5-tetramethyimidazoline-1-oxyl 3-oxide (PTIO) react with ·NO to form the corresponding iminonitroxides (PTIs) and $\cdot NO_2$. Under inflammatory conditions, ·NO is produced in much greater amount than normally, undergoing transformations which cause tissue damage, therefore the ·NO scavenger behaviour of nitronyl nitroxides is interesting to be used as potential therapeutic agents [1], [2].

2-(4-Carboxyphenyl)-4,4,5,5-tetramethyimidazoline-1-oxyl-3-oxide (cPTIO) is a compound similar to PTIO studied by some of us [5]. It has been shown that cPTIO exerts beneficial actions on systemic inflammatory response.

Some crystal phases of cPTIO have been described including co-crystals and salts [6], [7]. In the context of a study on cPTIO crystal phases, it is presented here the new crystal structure of the cPTIO perchlorate whose free radical nature has been stated by means of EPR. Suitable single crystals of cPTIO perchlorate (intense orange colour) have been studied using X-ray diffraction. Crystals are monoclinic ($P2_1/n$, Z=4) having the following unit-cell parameters: a=7.815(2), 20.736(4), 10.478(2) Å, β =91.83(3)º.

The comparison with cPTIO crystal structure [8] shows that N-O bond lengths are shorter (1.22 *vs.*1.30 Å) being the rest of bond distances very similar. The imidazoline ring is plane whereas in cPTIO adopts a half-chair conformation. The crystal packing is also different, in cPTIO, molecules are linked by COOH···O-N(nitroxide) H-bonding and form infinite zigzag chains whereas in the present structure, organic ion is surrounded by perchlorate groups and no chains are formed.

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X-ray powder diffraction study of malic acid

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The system of two malic acid enantiomers (components of the system) is typical example of a binary chiral system. It forms limited solid solutions as well as racemic modification at the equimolar composition [1]. Racemic malic acid is able to crystallize in different polymorphic modifications that complicates investigations of the system.

The molecule of malic acid $C_4H_6O_5$ (HOOC–CH_2–HCOH–COOH) has one chiral centre. Accordingly this compound can exist in the forms of two enantiomers *R* (+) and *S* (–). The database ICDD (Intern. Centre for Diffraction Data) contains characteristics of malic acid for its (–)-enantiomer ($P2_1$) and two monoclinic polymorph modifications of (*R,S*)-racemate ($P2_1/c$ и *Cc*). Referring to [2], (*R,S*)-malic acid grown from acetone solution is the stable modification, while that grown from water solution is the metastable modification. Unfortunately, these authors [2] did not indicate crystallochemical data (crystal system, space group, indices *hkl*, elementary cell parameters, etc.) for the phases of malic acid they synthesized.

We studied the polymorphic variety and structural deformations of racemic malic acid by means of X-ray and thermo-X-ray powder diffraction methods.

Initial samples of the enantiomers and racemate belong to the space groups $P2_1$ and $P2_1/c$ respectively. Besides, samples of malic acid obtained at different conditions were investigated at room temperature. Samples of the racemate (*R,S*), enantiomers (*R* and *S*), and mechanic mixture of the enantiomers (*R*+*S*) were grown from water, ethanol, and acetone solutions. Samples of the racemate (*R,S*) and equimolar mixture of enantiomers (*R*+*S*) were obtained after washing initial samples in heptane. Samples of crystallized melts of the racemate (*R,S*) and equimolar mixture of enantiomers (*R*+*S*) were obtained.

We found that (*R,S*)-malic acid could crystallize at least in three (probably in four) polymorph modifications: I ($P2_1/c$), II (*Cc*), III and supposedly IV (the space groups of III and IV ones were not identified for the present). Besides, X-ray characteristics (interplanar distances, *hkl* indices, parameters of monoclinic elementary cells, etc.) of two known (ICDD et al.) polymorphic modifications of racemic (*R,S*)-malic acid (I and II) were defined. Thermal phase transformations of *R*-enantiomer ($P2_1$), (*R,S*)-racemic modification I ($P2_1/c$), and equimolar mechanic mixture of malic acid (*R*+*S*) enantiomers were investigated at heating (the range was 50–140ºC, the temperature step was 2–10ºC). It was revealed that *R*-enantiomer and racemic modification I undergo only structural (thermal) deformations at heating: all the linear parameters *a*, *b*, and *c* (Å) and volume (Å^3) increase monotonously but angular parameter β decreases.