

## 09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

## 09.2-41 CRYSTAL STRUCTURES OF (-)-MALIC ACID AND OF A SECOND MODIFICATION OF (±)-MALIC ACID.

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(-)-Malic acid, in its ionized form, is one of the 4-carbon compounds that constitute the last stage of the citric acid cycle. Lenstra *et al.* [Doesburg & Lenstra, Bull. Soc. Chim. Belg. (1983) 92, 249; van Havere, Lenstra & Geise, Acta Cryst. (1980) B36, 3117, and references in these papers] have studied a series of salts of this biomolecule. The conformation of the malate ion appears to be dependent on the nature of the salt. Until lately no crystal-structure determination of malic acid was reported, presumably because of the difficulty in getting suitable crystals. Lenstra *et al.* [van Loock, van Havere & Lenstra, Bull. Soc. Chim. Belg. (1981) 90, 161] were the first to obtain single, albeit unstable, crystals of (±)-malic acid (I) suited to X-ray analysis. The space group is monoclinic,  $Aa$ ,  $Z=4$ .

Unexpectedly, in a standard way (*viz.* by slow evaporation of an aqueous solution) we recently obtained good quality crystals of a second modification of (±)-malic acid (II) and of (-)-malic acid (III). Although the space groups of (I) and (II) are different, the cell constants are practically the same.

In all three crystal structures the molecules have a planar C-chain. They form extended chains with the carboxyl groups interlinked by H bonds into cyclic pairs. The aliphatic OH group in (I) is considered to be free, whereas in (II) and (III) it serves as a donor.

(±)- $C_4H_5O_5$  (II),  $P2_1/c$ ,  $a=4.889(1)$ ,  $b=8.815(1)$ ,  $c=13.036(2)$  Å,  $\beta=102.93(1)^\circ$ ,  $V=547.6$  Å<sup>3</sup>,  $Z=4$ ,  $\lambda(MoK\alpha)=0.7107$  Å, 774 unique reflections [ $I > 2.5\sigma(I)$ ],  $R=0.049$ .  
 (-)- $C_4H_5O_5$ ,  $P2_1$ ,  $a=5.041(3)$ ,  $b=9.188(3)$ ,  $c=11.792(5)$  Å,  $\beta=94.06(4)^\circ$ ,  $V=544.8$  Å<sup>3</sup>,  $Z=4$ ,  $\lambda(MoK\alpha)=0.7107$  Å, 553 unique reflections [ $I > 2.5\sigma(I)$ ], current  $R=0.042$ .

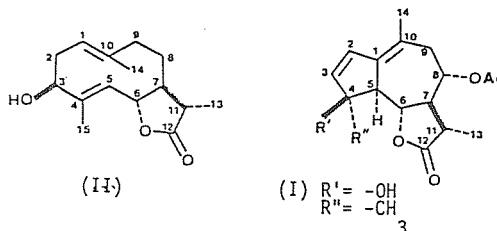
## 09.2-42 THE STRUCTURES OF ANION-RADICAL SALTS:

$C_2H_7N_2S$ -TCNQ AND  $C_2H_7N_2Se$ -TCNQ.  
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The crystal structures of a new series of TCNQ salts with S-methyl-thiuronium ( $MT = C_2H_7N_2S$ ) and Se-methyl-selenouronium ( $MS = C_2H_7N_2Se$ ) cations have been determined. X-ray diffraction data were collected on a Syntex  $P2_1$  diffractometer with  $MoK\alpha$  radiation. The structure was solved by Patterson methods, and full-matrix refinement was carried out using XTL program packages. Atoms S and Se were located by the heavy atom method. The remaining C, N and H were located by means of Fourier and difference Fourier syntheses. The compounds crystallise in the monoclinic space group  $P2_1/c$  with:  $MT$ -TCNQ,  $a = 11.005(2)$ ,  $b = 12.305(3)$ ,  $c = 11.112(3)$  Å,  $\beta = 100.98(2)^\circ$ ,  $v = 1482.2$  Å<sup>3</sup>,  $Z = 4$ ,  $D = 1.32$  gcm<sup>-3</sup>, final residual  $R = 0.046$ ;  $MS$ -TCNQ,  $a = 10.984(2)$ ,  $b = 12.269(2)$ ,  $c = 11.191(2)$  Å,  $\beta = 100.94(1)^\circ$ ,  $v = 1480.9$  Å<sup>3</sup>,  $Z = 4$ ,  $D = 1.53$  gcm<sup>-3</sup>,  $R = 0.053$ . The TCNQ ions are planar, the cyan-groups  $-C(CN)_2$  being rotated by  $4-6^\circ$  from the plane of the quinonoid ring. The bond length distribution in the TCNQ ions corresponds to the pseudo-aromatic type: all double bonds are lengthened by  $0.51-0.53$  Å, and ordinary bonds are shortened. From the structures and bond distribution analysis the compounds are shown to be simple ion-radical TCNQ salts with full charge transfer and discrete anion pair stacking. The mean interplanar distance between TCNQ molecules is about 3.40 Å.

## 09.2-43 Structure and Conformation of a Stoichiometric Adduct of 4-Epimatricin with 3β-Hydroxydihydrocostunolide and of 4-Epimatricin alone.

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The guaianolide 4-Epimatricin and the gemmacrolide 3β-Hydroxydihydrocostunolide (I and II respectively) form in the solid state a stoichiometric non-covalent adduct through complex chain of hydrogen bonding involving their hydroxyl groups and one water molecule. 3β-Hydroxydihydrocostunolide exists in the solid state as a  $[{}^{15}D_5, {}^I D^{14}]$  chair-chair rotamer, whilst the cycloheptene ring of 4-epimatricin adopts a  $C_s$  conformation. Comparison of the crystal structures of the latter compound alone and in the adduct reveals a somewhat different conformation of the γ-lactone ring and a larger deviation from the ideal  $C_s$  symmetry of the cycloheptene ring in the adduct.