09.2.41 STRUCTURE OF (-)-MALIC ACID AND OF A SECOND MODIFICATION OF (+)-MALIC ACID.


(-)-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. [Doeburg & Lenstra, Bull. Soc. Chim. Belg. (1983) 92, 249; van Haveren, 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 recently no crystal-structure determination of malic acid was reported, presumably because of the difficulty in getting suitable crystals. Lenstra et al. [van Loock, van Haveren & Lenstra, Bull. Soc. Chim. Belg. (1981) 90, 101] were the first to obtain single, albeit unstable, crystals of (-)-malic acid (I) suited to X-ray analysis. The space group is monoclinic, $Aa_2$, $Z=2$.

Unexpectedly, in a standard way (i.e., 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 O-chain. They form extended chains with the cyanogen 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.

The TCNQ ions are planar, the cyanogen groups being rotated by 4-6° 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 in-plane distance between TCNQ molecules is about 3.40 Å.

09.2.42 THE STRUCTURES OF ANION-RADICAL SALTS: $C_6H_5N_2Se-TCNO$ AND $C_6H_5N_2S-TCNO$


The crystal structures of a new series of TCNQ salts with S-methyl-thiouronium (MT = $C_6H_5N_2S$) and Se-methyl-selenouronium (MS = $C_6H_5N_2Se$) cations have been determined. X-ray diffraction data were collected on a Syntax P2$_3$ diffractometer with MoK$_\alpha$ radiation. The structure was solved by Patterson methods, and full-matrix refinement was carried out using XINT programs. 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, $a = 11.005(2)$, $b = 12.305(2)$, $c = 13.036(2)$, $\alpha = 102.93(1)°$, $\beta = 89.07(3)°$, $\gamma = 118.36(1)°$, $V = 1482.2$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.32$ g cm$^{-3}$, $R_{\text{index}} = 0.049$. MS-TCNQ, $a = 11.121(3)$, $b = 10.984(2)$, $c = 12.269(3)$, $\alpha = 119.12(1)°$, $V = 1482.2$ Å$^3$, $Z = 4$, $D_{\text{calc}} = 1.32$ g cm$^{-3}$, $R_{\text{index}} = 0.053$. The TCNQ ions are planar, the cyanogen groups being rotated by 4-6° 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 in-plane distance between TCNQ molecules is about 3.40 Å.

The guaianolide 4-epimaticrin and the germacrolide 3 $\beta$-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. 3 $\beta$- Hydroxydihydrocostunolide exists in the solid state as a 15$\beta$, 14$\alpha$ chair-chair rotation, whilst the cycloheptene ring of 4-epimaticrin adopts a C$_2$ conformation. Comparison of the crystal structures of the latter compound alone and in the adduct reveals a somewhat different conformation of the y-lactone ring and a larger deviation from the ideal C$_2$ symmetry of the cycloheptene ring in the adduct.