

09. STRUCTURES OF ORGANIC, ORGANOMETALLIC AND COORDINATION COMPOUNDS

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

By *P. van der Sluis & J. Kroon*, Laboratorium voor Kristal en Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands.

(-)-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, $\beta=102.93(1)^\circ$, $V=547.6$ Å³, $Z=4$, $\lambda(MoK\alpha)=0.7107$ 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, $\beta=94.06(4)^\circ$, $V=544.8$ Å³, $Z=4$, $\lambda(MoK\alpha)=0.7107$ Å, 553 unique reflections [$I > 2.5\sigma(I)$], current $R=0.042$.

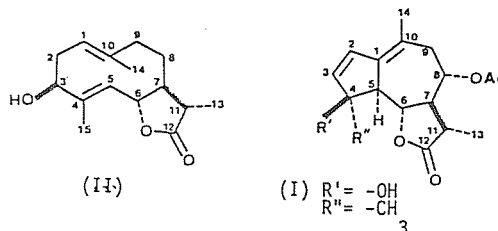
09.2-42 THE STRUCTURES OF ANION-RADICAL SALTS:

$C_2H_7N_2S$ -TCNQ AND $C_2H_7N_2Se$ -TCNQ.
 By *G.C. Abashev, R.M. Vlasova, N.F. Kartenko, A.M. Kuzmin, I.V. Rozhdestvenskaya, V.N. Semkin, O.A. Usov and V.S. Russkikh, A.F. Ioffe Physico-Technical Institute, 194021 Leningrad, U.S.S.R.*

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, $\beta = 100.98(2)^\circ$, $v = 1482.2$ Å³, $Z = 4$, $D = 1.32$ gcm⁻³, final residual $R = 0.046$; MS -TCNQ, $a = 10.984(2)$, $b = 12.269(2)$, $c = 11.191(2)$ Å, $\beta = 100.94(1)^\circ$, $v = 1480.9$ Å³, $Z = 4$, $D = 1.53$ gcm⁻³, $R = 0.053$. 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.

G. Appendino, Istituto di Chimica Farmaceutica, Facoltà di Farmacia, Corso Raffaello 31, IOI25 Torino
 M. Calleri and G. Chiari, Dipartimento di Scienze della Terra, Via San Massimo 22, IOI23, Torino
 and D. Viterbo, Istituto di Chimica Fisica dell'Università, Corso M. d'Azeglio 48, IOI25, Torino, Italy.



The guaianolide 4-Epimatricin and the germacrolide 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 $\left[\begin{matrix} 15 \\ D_5 \end{matrix} , \begin{matrix} I \\ D^{I4} \end{matrix} \right]$ 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.