Crystal data on ortho-substituted benzaldehydes. By Marcel Baiwir and Gabriel Llabres, Institut de Physique, Université de Liège au Sart Tilman, 4000 Liège, B-Belgium and Jean-Louis Piette, Institut de Chimie organique, Université de Liège, 4000 Liège, B-Belgium

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Unlike the position with negatively charged substituents, little has been done on benzaldehydes ortho-substituted with positively charged groups. This is more especially true in the field of crystallography where only the X-ray and neutron diffraction study of o-nitrobenzaldehyde has been reported [Coppens & Schmidt, Acta Cryst. (1964). 17, 222–228; Coppens, Acta Cryst. (1964). 17, 573–578]. Preliminary results of a structural investigation on Se- and Te-containing benzaldehydes are presented. The main purpose is to corroborate and to complete the conclusion of recent n.m.r. work on the conformation of these molecules [Baiwir, Llabres, Denoel & Piette, Mol. Phys. (1973). 25, 1–7]. The following compounds have been studied: C₆H₄·COH·TeCl, C₆H₄·COH·TeBr, C₆H₄·COH·TeI, C₆H₄·COH·SeCl, C₆H₄·COH·SeBr. The crystal structure of the second (TeBr) has been recently reported [Baiwir Llabres, Dideberg, Dupont & Piette, Acta Cryst. (1974). B30, 139–143] and the structure of the last (SeBr) is presently in the final stage of refinement.

Origin of specimens

The studied compounds were synthesized in our laboratories. The specimens were crystallized from saturated solutions in ethanol by slow evaporation at room temperature. The crystal data were obtained from Weissenberg photographs (TeCl, TeI, SeCl) and from Hilger and Watts diffractometer measurements (TeBr, SeBr). In both cases, the Cu Kα radiation was used.

Crystal data

O-Formyl phenyl tellurenyl chloride (C₆H₄·COH·TeCl)

Crystal geometry

Laue Class: orthorhombic
Space group: undetermined (see Discussion)

a = 10.41 (4) Å  \( V = 807 \text{ Å}^3 \)
b = 4.33 (2) \( Z = 4 \)
c = 17.08 (3) \( D_x = 2.37 \text{ g cm}^{-3} \).

Crystal physics

Colour: dark red;
melting point: 94°C.

O-Formyl phenyl tellurenyl bromide (C₆H₄·COH·TeBr)

Crystal geometry

Laue class: monoclinic
Space group: P2₁/c

a = 12.253 (3) Å  \( \beta = 102.48 ° \)
b = 5.839 (3) \( V = 813 \text{ Å}^3 \)
c = 11.706 (3) \( D_x = 2.538 \text{ g cm}^{-3} \).

Crystal physics

Colour: dark red;
melting point: 119°C.

O-Formyl phenyl tellurenyl iodide (C₆H₄·COH·TeI)

Crystal geometry

Laue class: monoclinic
Space group: P2₁/c

a = 11.99 (3) Å  \( \beta = 102° \)
b = 6.07 (3) \( V = 829 \text{ Å}^3 \)
c = 11.65 (3) \( D_x = 2.88 \text{ g cm}^{-3} \).

Crystal physics

Colour: dark red;
melting point: 119°C.

Discussion

The TeCl derivative crystallizes as a superstructure. In fact, the true unit cell is 16 times larger than quoted above, as can be seen from (hkl) and (h0l) Weissenberg photographs. Moreover, the Weissenberg lines indicate a mobility of the molecule in a plane perpendicular to the b axis: this ability to move accounts for the superstructural cell.

Isostructural relations are evident between, on one hand, the TeBr and Tel derivatives and, on the other hand, the SeBr and SeCl ones. Then we may conclude that all these compounds adopt a cis configuration in solution (n.m.r. measurements) as well as in the crystal (X-ray measurements).

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