Crystal Structure and Cationic Motion of *o*-Toluidinium Chloranilate and *m*-Toluidinium Chloranilate Studied by X-ray Diffraction and ^{1}H NMR

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Z. Naturforsch. **58a,** 631 – 637 (2003); received August 5, 2003

The crystal structure of *o*-toluidinium chloranilate and *m*-toluidinium chloranilate, $2CH_3C_6H_4NH_3^+ \cdot C_6O_4Cl_2^{2-}$, was determined by single crystal X-ray diffraction at room temperature. It was found that *o*-toluidinium chloranilate (I) is monoclinic, $P2_1/n$ (#14), $Z = 2$, $a = 5.2184(14)$, $b = 7.825(2)$, $c = 22.840(5)$ Å, and $\beta = 92.015(19)^\circ$, and *m*-toluidinium chloranilate (II) is monoclinic, $P2_1/c$ (#14), $Z = 2$, $a = 11.214(2)$, $b = 5.4844(10)$, $c = 16.379(6)$ Å, and $\beta = 105.21(2)^\circ$. In these salts, the cations are connected with the anions by N-H…O hydrogen bonds to form 2:1 units of $2CH_3C_6H_4NH_3^+ \cdot C_6O_4Cl_2^{2-}$ that are located on inversion centers. The $2CH_3C_6H_4NH_3^+ \cdot C_6O_4Cl_2^{2-}$ units in both salts are connected by other N-H…O hydrogen bonds to build a three-dimensional hydrogen-bond network. Motions of the toluidinium ions in solid (I) and (II) were studied by ^{1}H NMR spin-lattice relaxation time measurements. Reorientations of the NH_3^+ group about the C-N bond axis and the CH_3 group about the C-C bond axis were observed, and their motional parameters were evaluated. The internal rotational barriers of the NH_3^+ and CH_3 groups of an isolated *o*-toluidinium ion were estimated from *ab initio* molecular orbital calculations at HF/6-31G(d,p), MP2/6-31G(d,p), and B3LYP/6-31G(d,p) levels of theory.

Key words: Crystal Structure; X-ray Diffraction; Hydrogen Bond; Cationic Motion; MO Calculation.