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

Takeo Fukunaga, Naoki Kumagae, and Hiroyuki Ishida

Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan

Reprint requests to Prof. H. I.; Fax +81-86-251-7832; E-mail: ishidah@cc.okayama-u.ac.jp

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The crystal structure of o-toluidinium chloranilate and m-toluidinium chloranilate, 2C₆H₄C₆H₄NH₃⁺·C₆O₄Cl²⁻, was determined by single crystal X-ray diffraction at room temperature. It was found that o-toluidinium chloranilate (I) is monoclinic, P2₁/n (#14), Z = 2, a = 5.2184(14), b = 7.825(2), c = 22.840(5) Å, and β = 92.015(19)°, and m-toluidinium chloranilate (II) is monoclinic, P2₁/c (#14), Z = 2, a = 11.214(2), b = 5.4844(10), c = 16.379(6) Å, and β = 105.21(2)°. In these salts, the cations are connected with the anions by N-H...O hydrogen bonds to form 2:1 units of 2C₆H₄C₆H₄NH₃⁺·C₆O₄Cl²⁻ that are located on inversion centers. The 2C₆H₄C₆H₄NH₃⁺·C₆O₄Cl²⁻ 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 1H NMR spin-lattice relaxation time measurements. Reorientations of the NH₃⁺ group about the C-N bond axis and the CH₃ group about the C-C bond axis were observed, and their motional parameters were evaluated. The internal rotational barriers of the NH₃⁺ and CH₃ 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.