Crystal Structure of Lutidinium Chloranilates

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The crystal structure of four lutidinium chloranilates, $(CH_3)_2C_6H_3NH^+ \cdot C_6HO_4Cl_2^-$, was determined by single crystal X-ray diffraction at room temperature. 2,4-lutidinium chloranilate (I): triclinic, *P*1 (#2), *Z* = 2, *a* = 11.401(2), *b* = 11.639(2), *c* = 5.1588(8) Å, α = 91.899(15)°, β = 90.104(14)°, and γ = 83.355(16)°, 2,5-lutidinium chloranilate (II): monoclinic, $P2_1/c$ (#14), *Z* = 4, *a* = 7.709(2), *b* = 11.294(2), *c* = 15.572(3) Å, and β = 95.54(2)°, 2,6-lutidinium chloranilate (III): triclinic, *P*1 (#2), *Z* = 2, *a* = 9.1312(17), *b* = 9.127(2), *c* = 9.1108(13) Å, α = 93.027(17)°, β = 110.766(13)°, and γ = 105.206(17)°, 3,4-lutidinium chloranilate (IV): monoclinic, $P2_1/c$ (#14), *Z* = 4, *a* = 10.6356(15), *b* = 5.1896(5), *c* = 24.528(3) Å, and β = 95.807(10)°. In these salts, the hydrogen chloranilate monoanions are present as a hydrogen-bonded dimer which has an inversion center. The lutidinium ions are linked on both sides of the dimer via N-H...O hydrogen bonds. Hydrogen bonding patterns in the chloranilic acid-amine (1:1) systems are discussed based on the present crystallographic data and those retrieved mainly from CSD. The patterns can be classified into three types depending on the shape of the amine molecules. Molecular orbital calculations at HF/6-311+G(d,p), MP2/6-311+G(d,p), and B3LYP/6-311+G(d,p) levels of theory were carried out to compare the molecular structure of chloranilic acid with those of its monoanion and dianion.

Key words: Crystal Structure; X-ray Diffraction; Hydrogen Bond; HF.