Crystal structure of anilinium perchlorate, $C_6H_5NH_3^+ClO_4^-$

J. A. Paixão, A. Matos Beja, M. Ramos Silva, L. Alte da Veiga

Universidade de Coimbra, Faculdade de Ciências e Tecnologia, Departamento de Física, P-3000 Coimbra, Portugal

and J. Martin-Gil

ETSII, Departamento de Química Inorgánica, Paseo del Cauce, s/n, SP-47011 Valladolid, Spain

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Abstract

$C_6H_5ClNO_4$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 5.895(3)$ Å, $b = 7.505(5)$ Å, $c = 18.909(7)$ Å, $V = 836.6$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.039$, $R_w(F^2) = 0.092$, $T = 293$ K.

Source of material

The title compound was prepared by reacting an aqueous solution of *N,N'*-diphenylformamidine (98%, Aldrich) with perchloric acid and the precipitate was solubilized in ethanol. [Caution: perchlorates are potential explosives!]. Violet, large single crystals of prismatic form grew from the solution, by slow evaporation, over a period of a few days from which one small piece was cut and used for the X-ray analysis.

The H-atoms of the phenyl ring were placed at calculated positions and refined as riding using the SHELXL-97 defaults: $C(\text{aryl})-H = 0.93$ Å, $U(H)_{\text{eq}} = 1.2U_{\text{eq}}$ of the parent C atom [1]. A difference Fourier map revealed that the NH_3^+ group exhibits rotational disorder. Instead of well defined peaks for the hydrogen atoms, a ring of uniform residual density was observed. Although it is possible that the NH_3^+ group is rotating rather freely at room temperature, we tried to model this residual density assuming that the disorder corresponds to two alternate positions. The conformation of one of the disordered NH_3^+ groups was chosen such that one H atom is eclipsed with the ring (the most commonly found conformation in anilinium salts) and the other NH_3^+ group is rotated from this position by 60° around the C–N bond, so that the positions of the H atoms define a regular hexagon. A single isotropic displacement parameter $U(H) = 1.5U_{\text{eq}}(N)$ was assigned to the six H atoms. The occupation of these two groups was refined with one free variable such that the two occupations were constrained to add up to unity. The refined values are 0.54(4) 0.46(4).

Discussion

The N–H distance was allowed to change during refinement and was converged to 0.83 Å. The intramolecular bond distances and angles of the anilinium cation are in good agreement with literature data [2–5]. The ring is planar within 0.002 Å but the N atom deviates by $-0.025(6)$ Å from the least squares plane. There are small differences in the aromatic C–C bond length and endocyclic bond angles of the phenyl ring expected from the σ -electron withdrawing character of the NH_3^+ group. The C1–N distance [1.466(3) Å] and the C6–C1–C2 angle ipso to the N atom [121.9(3)°] are in good agreement with the average values [1.462(2) Å and 121.7(2)°] [6] for the anilinium cation. The geometry of the anion is unexceptional. The average Cl–O [1.413(8) Å] distance and O–Cl–O angle [109.5(7)°] are comparable to those observed in other perchlorate salts [7]. There are no solvent-accessible voids in the crystal lattice.

Table 1. Data collection and handling.

Crystal:	light violet, prismatic, size 0.15 x 0.24 x 0.37 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	4.31 cm ⁻¹
Diffraction, mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	55.16°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	2210, 1931
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 1334
$N(\text{param})_{\text{refined}}$:	111
Programs:	SHELXL-97 [1], XCAD4 [9], SDP [10], ORTEPII [12], SHELXS-97 [12]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{iso}
H(1A)	4a	0.54(4)	0.866(3)	0.598(1)	0.5633(4)	0.079
H(1B)	4a	0.54	0.634(3)	0.604(1)	0.5636(4)	0.079
H(1C)	4a	0.54	0.7434(9)	0.443(3)	0.5668(3)	0.079
H(1D)	4a	0.46 (4)	0.629(3)	0.499(1)	0.5658(4)	0.079
H(1E)	4a	0.46	0.862(3)	0.493(1)	0.5655(4)	0.079
H(1F)	4a	0.46	0.7517(9)	0.654(3)	0.5623(5)	0.079
H(2)	4a		1.0513	0.6872	0.6640	0.061
H(3)	4a		1.0531	0.6973	0.7868	0.072
H(4)	4a		0.7606	0.5808	0.8502	0.072
H(5)	4a		0.4564	0.4520	0.7930	0.071
H(6)	4a		0.4500	0.4386	0.6705	0.061

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Cl	4a	0.2574(2)	0.52553(8)	0.96647(4)	0.0597(4)	0.0375(3)	0.0440(3)	−0.0020(7)	0.0001(7)	0.0055(3)
O(1)	4a	0.258(1)	0.6728(3)	0.9208(2)	0.119(2)	0.050(1)	0.098(2)	−0.001(3)	0.009(4)	0.030(1)
O(2)	4a	0.0558(6)	0.4257(5)	0.9539(2)	0.068(2)	0.077(3)	0.093(3)	−0.022(2)	0.002(2)	−0.005(2)
O(3)	4a	0.2676(9)	0.5772(5)	1.0383(1)	0.107(2)	0.131(3)	0.050(1)	0.009(3)	−0.004(3)	−0.025(2)
O(4)	4a	0.4500(6)	0.4133(5)	0.9505(2)	0.071(2)	0.058(2)	0.091(3)	0.015(2)	0.007(2)	0.000(2)
N	4a	0.7478(9)	0.5505(3)	0.5793(1)	0.073(2)	0.041(1)	0.044(1)	0.005(3)	−0.002(3)	−0.0004(9)
C(1)	4a	0.7492(9)	0.5610(3)	0.6568(1)	0.047(2)	0.030(1)	0.039(1)	0.002(2)	−0.001(3)	0.0002(9)
C(2)	4a	0.9318(7)	0.6395(5)	0.6899(2)	0.047(2)	0.046(2)	0.059(2)	−0.006(2)	−0.000(2)	0.002(2)
C(3)	4a	0.9316(8)	0.6452(5)	0.7632(2)	0.064(2)	0.055(2)	0.062(2)	0.001(2)	−0.021(2)	−0.011(2)
C(4)	4a	0.758(1)	0.5761(4)	0.8010(2)	0.078(2)	0.058(2)	0.044(2)	0.018(3)	−0.008(3)	0.000(1)
C(5)	4a	0.5761(7)	0.4988(5)	0.7669(2)	0.060(2)	0.058(2)	0.059(2)	0.003(2)	0.016(2)	0.012(2)
C(6)	4a	0.5717(6)	0.4909(5)	0.6939(2)	0.047(2)	0.048(2)	0.057(2)	−0.006(2)	−0.006(2)	0.001(2)

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