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Crystal structure of (*E*)-4-((4-chlorophenylimino) methyl)pyridinium 3,5-dinitrobenzoate, $C_{19}H_{13}ClN_4O_6$

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.35 × 0.31 × 0.24 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.26 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	23587, 4595, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4077
$N(\text{param})_{\text{refined}}$:	271
Programs:	Bruker [1], SHELX [2, 4], Mercury [3]

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Abstract

$C_{19}H_{13}ClN_4O_6$, monoclinic, $P2_1/n$ (no. 14), $a = 4.8032(1)$ Å, $b = 19.5545(5)$ Å, $c = 19.6915(6)$ Å, $\beta = 90.640(1)^\circ$, $V = 1849.39(8)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0369$, $wR_{\text{ref}}(F^2) = 0.1011$, $T = 100(2)$ K.

CCDC no.: 1976390

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The Schiff base (*E*)-*N*-(4-chlorophenyl)-1-(pyridin-4-yl) methanimine was synthesized using a solvent free grinding

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.24030(7)	0.17151(2)	0.22774(2)	0.02373(10)
O1	−0.6861(2)	−0.15929(6)	0.88344(6)	0.0303(3)
O2	−1.0191(2)	−0.14248(5)	0.95467(5)	0.0266(2)
O3	−1.4605(2)	0.07664(5)	0.96821(5)	0.0245(2)
O4	−1.3363(2)	0.15901(5)	0.90140(6)	0.0275(2)
O5	−0.6239(2)	0.11936(6)	0.72800(5)	0.0290(2)
O6	−0.3923(2)	0.02022(6)	0.73132(5)	0.0276(2)
N1	−0.8627(3)	−0.12316(6)	0.90962(6)	0.0207(2)
N2	−1.3163(2)	0.10035(6)	0.92263(6)	0.0194(2)
C1	−0.5720(3)	0.05961(7)	0.75157(7)	0.0200(3)
C2	−0.7529(3)	0.03677(7)	0.81005(6)	0.0185(3)
C3	−0.7222(3)	−0.02998(7)	0.83349(7)	0.0190(3)
H3A	−0.588469	−0.059708	0.814061	0.023*
C4	−0.8907(3)	−0.05222(7)	0.88575(7)	0.0183(3)
C5	−1.0871(3)	−0.01087(7)	0.91609(6)	0.0178(3)
H5	−1.201508	−0.027042	0.951712	0.021*
C6	−1.1080(3)	0.05523(7)	0.89178(6)	0.0175(3)
C7	−0.9479(3)	0.08027(7)	0.83905(6)	0.0183(3)
H7	−0.970819	0.125824	0.823184	0.022*
N3	−0.3050(3)	0.13949(7)	0.62705(6)	0.0233(3)
H3	−0.418643	0.132159	0.661030	0.028*
N4	0.4151(3)	0.13075(6)	0.44523(6)	0.0209(2)
C8	−0.2935(3)	0.20121(7)	0.59871(7)	0.0219(3)
H8	−0.411018	0.236564	0.614904	0.026*
C9	−0.1129(3)	0.21478(7)	0.54600(7)	0.0210(3)
H9	−0.105578	0.259140	0.526427	0.025*
C10	0.0573(3)	0.16282(7)	0.52204(7)	0.0190(3)

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C11	0.0382(3)	0.09823(8)	0.55152(7)	0.0249(3)
H11	0.149314	0.061523	0.535580	0.030*
C12	−0.1447(3)	0.08833(8)	0.60424(8)	0.0281(3)
H12	−0.157379	0.044488	0.624759	0.034*
C13	0.2526(3)	0.17694(7)	0.46668(7)	0.0194(3)
H13	0.257027	0.221175	0.446774	0.023*
C14	0.6074(3)	0.14498(7)	0.39310(7)	0.0191(3)
C15	0.6740(3)	0.21052(7)	0.36949(7)	0.0228(3)
H15	0.586773	0.249484	0.388681	0.027*
C16	0.8670(3)	0.21873(7)	0.31817(7)	0.0223(3)
H16	0.909986	0.263031	0.301474	0.027*
C17	0.9961(3)	0.16144(7)	0.29162(7)	0.0193(3)
C18	0.9382(3)	0.09634(7)	0.31485(7)	0.0211(3)
H18	1.030379	0.057670	0.296454	0.025*
C19	0.7423(3)	0.08864(7)	0.36569(7)	0.0202(3)
H19	0.699963	0.044150	0.381974	0.024*

of 4-pyridinecarboxaldehyde and 4-chloroaniline [5]. 0.05 mmol of the Schiff base were added to a stirred solution containing magnesium acetate tetrahydrate (0.5 mmol) and 3,5-dinitrobenzoic acid (1 mmol) in ethanol (10 mL) for 6 hours. Slow evaporation of the ethanolic solution led to the formation of X-ray quality, yellow block-shaped crystals of the title compound after three days. **Yield** = 81%; **m.p.** = 155–157 °C; **¹H-NMR** (*d*₆DMSO, 400 MHz): δ (ppm) 7.36 (2H, q, *J* = 2.88 Hz), 7.49 (2H, q, *J* = 2.88 Hz), 7.84 (2H, d, *J* = 5.76 Hz), 8.69 (1H, s), 8.76 (2H, d, *J* = 4.44 Hz), 8.90 (2H, d, *J* = 2.16 Hz), 9.00 (1H, t, *J* = 2.12 Hz). **¹³C-NMR** (*d*₆DMSO, 400 MHz): δ (ppm) 115.67, 122.34, 122.59, 122.71, 123.52, 128.92, 129.33, 129.70, 131.71, 135.17, 142.76, 148.77, 149.76, 150.92, 151.55, 164.43, 193.80.

Experimental details

A Bruker Smart APEX2 diffractometer with Mo *K*α radiation was used for crystal evaluation and data collection [1]. The structure was solved by the direct method using the SHELXS [2] program and refined. The visual crystal structure information was performed using Mercury [3] system software. All non-hydrogen atoms were refined isotropically and then by anisotropic refinement with full-matrix least squares method based on *F*² using SHELXL [4]. All C—H_{aromatic} and N—H bond distances were constrained using the appropriate HFIX commands and *U*_{iso} set to 1.2*U*_{eq} of the parent atom.

Comment

Schiff bases are condensation products of the reaction of carbonyl compounds (aldehyde or ketones) and amines. They were first isolated by Hugo Schiff in 1864 [6]. Their ability to stabilize metal centers at different oxidation state affords them versatility in biological application and co-ordination

chemistry [7, 8]. Benzoic acid derivatives have been used as co-ligands for the formation of heteroleptic complexes [9–11].

The asymmetric unit of the title compound comprises of an anionic 3,5-dinitrobenzoate and a cationic (*E*)-4-((4-chlorophenylimino)methyl)pyridinium species. The pyridinium and aniliny rings of the cationic species are not coplanar and have a dihedral angle of 10.37(7)°. On the other hand, the dihedral angle between each of the *meta*-nitro groups and the phenyl ring of the anionic species ranged from 1.04(8)° to 1.99(9)° which is narrower than that of the carboxylate group (5.4872(1)°). This could be attributed to the electrostatic effect including the intermolecular N3—H3···O5 (N3···O5 = 2.5535(15) Å; H3···O5 = 1.674 Å; N3—H3···O5 = 178°) and C12—H12···O6 [C12···O6 = 3.0849(18) Å; H12···O6 = 2.440 Å; C12—H12···O6 = 125°] hydrogen bonding patterns which exists between the carboxylate and pyridinium moieties that are similar to a closely related compound in literature [12].

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