

2-(4-Chlorophenyl)-5-methyl-6,7,8,9,10,11-hexahydrocycloocta[e][1,3]oxazolo[3,2-a]-pyridin-12-ium perchlorate

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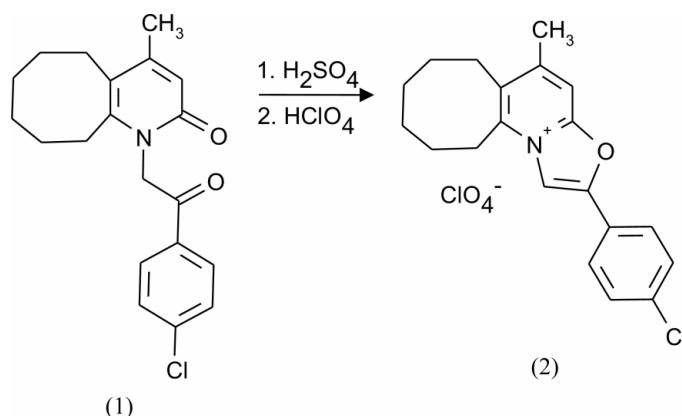
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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.004$ Å
 R factor = 0.045
 wR factor = 0.124
Data-to-parameter ratio = 15.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The title compound, $\text{C}_{20}\text{H}_{21}\text{ClNO}^+\cdot\text{ClO}_4^-$, was synthesized and characterized by ^1H NMR and X-ray diffraction techniques.Received 9 June 2004
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Comment

In the course of systematic investigations of the size effect of cycloalkane fragments on the reactivity of the corresponding heterocycles based on pyridine, we have previously described the crystal structure of 1-(4-chlorophenacyl)-4-methyl-5,6,7,8,9,10-hexahydrocycloocta[*b*]pyridin-2(1*H*)-one, (1) (Albov *et al.*, 2004*a*). Following a study with cyclohexene derivatives (Albov *et al.*, 2004*b*), we synthesized the title compound, (2).

An analysis of bond lengths in the oxazolopyridinium ring system of (2) (Fig. 1 and Table 1) reveals that the pyridinium fragment is certainly aromatic while the N1/C5 chain shows weaker delocalization. The positive charge is located on the N1 atom. The nine-membered bicyclic system is planar to within 0.0218 (19) Å, with atoms C11, C16 and C17 lying in the same plane; atom C10 is displaced from this plane by 0.125 (4) Å. The dihedral angle between the oxazolopyridinium and benzene fragments is 5.33 (15)°, indicating that there is considerable conjugation between these aromatic fragments.

All these results will be compared with the crystal structures of five-membered cycloalkane derivatives currently in progress, as well as with published (Albov *et al.*, 2004*b,c*) six- and seven-membered cycloalkane derivatives.

Experimental

Compound (1) (2.64 g) was dissolved in 20 ml of sulfuric acid and allowed to stand overnight. The solution then was poured into 100 ml of 3% aqueous solution of perchloric acid. A white precipitate formed and the mixture was kept overnight again for complete

precipitation. The product was filtered off and washed with water and acetone (yield 3.20 g, 98%). It was recrystallized from acetonitrile (m.p. 584 K with explosion). ¹H NMR (DMSO-*d*₆, 400 MHz, p.p.m.): 1.64 (*m*, 4H, 13-CH₂ + 14-CH₂), 1.79 (*m*, 2H, 12-CH₂), 1.97 (*m*, 2H, 15-CH₂), 2.64 (*s*, 3H, 10-CH₃), 3.01 (*t*, 2H, 11-CH₂), 3.41 (*t*, 2H, 16-CH₂), 7.69, 7.95 (*dd*, 4H, Ar), 8.11 (*s*, 1H, 6-CH), 9.52 (*s*, 1H, 2-CH).

Crystal data

C₂₀H₂₁ClNO⁺·ClO₄⁻
M_r = 426.28
 Monoclinic, *P*2₁/*c*
a = 7.8301 (9) Å
b = 18.6827 (19) Å
c = 13.8840 (14) Å
 β = 103.013 (9)°
V = 1978.9 (4) Å³
Z = 4

D_x = 1.431 Mg m⁻³
 Cu K α radiation
 Cell parameters from 25 reflections
 θ = 30–34°
 μ = 3.23 mm⁻¹
T = 293 (2) K
 Prism, colourless
 0.26 × 0.24 × 0.21 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 Non-profiled $\omega/2\theta$ scans
 Absorption correction: none
 3977 measured reflections
 3977 independent reflections
 2581 reflections with *I* > 2 σ (*I*)

θ_{\max} = 74.9°
h = -9 → 9
k = 0 → 23
l = 0 → 17
 1 standard reflection
 frequency: 60 min
 intensity decay: 2%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.045
wR (*F*²) = 0.124
S = 0.93
 3977 reflections
 254 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0584P)^2]$,
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C11–C20	1.740 (3)	C11–C12	1.529 (4)
N1–C5	1.358 (3)	C12–C13	1.503 (4)
N1–C9	1.392 (3)	C13–C14	1.439 (5)
N1–C2	1.413 (3)	C14–C15	1.560 (5)
C2–C3	1.323 (3)	C15–C16	1.493 (4)
C3–O4	1.383 (3)	C17–C18	1.378 (3)
C3–C17	1.453 (3)	C17–C22	1.392 (3)
O4–C5	1.360 (3)	C18–C19	1.377 (4)
C5–C6	1.354 (3)	C19–C20	1.384 (4)
C6–C7	1.397 (4)	C20–C21	1.377 (4)
C7–C8	1.397 (4)	C21–C22	1.378 (4)
C7–C10	1.493 (3)	C12–O23	1.344 (3)
C8–C9	1.363 (4)	C12–O21	1.394 (3)
C8–C11	1.517 (4)	C12–O22	1.409 (3)
C9–C16	1.482 (4)	C12–O24	1.412 (3)
C5–N1–C9	121.2 (2)	C8–C9–N1	116.6 (2)
C5–N1–C2	106.75 (19)	C8–C9–C16	127.4 (3)
C9–N1–C2	132.0 (2)	N1–C9–C16	116.0 (2)
C3–C2–N1	107.2 (2)	C8–C11–C12	112.6 (2)
C2–C3–O4	110.2 (2)	C13–C12–C11	115.5 (3)
C2–C3–C17	132.2 (2)	C14–C13–C12	115.8 (3)
O4–C3–C17	117.5 (2)	C13–C14–C15	118.7 (3)
C5–O4–C3	106.34 (18)	C16–C15–C14	114.9 (3)
C6–C5–N1	122.7 (2)	C9–C16–C15	114.7 (3)
C6–C5–O4	127.8 (2)	C18–C17–C3	121.6 (2)
N1–C5–O4	109.50 (19)	C22–C17–C3	119.7 (2)
C5–C6–C7	117.8 (3)	O23–C12–O21	105.0 (2)
C6–C7–C8	119.1 (2)	O23–C12–O22	110.1 (3)
C6–C7–C10	117.5 (3)	O21–C12–O22	108.3 (2)
C8–C7–C10	123.4 (3)	O23–C12–O24	108.2 (2)
C9–C8–C7	122.6 (3)	O21–C12–O24	109.9 (2)
C9–C8–C11	117.7 (3)	O22–C12–O24	115.0 (2)
C7–C8–C11	119.7 (2)		

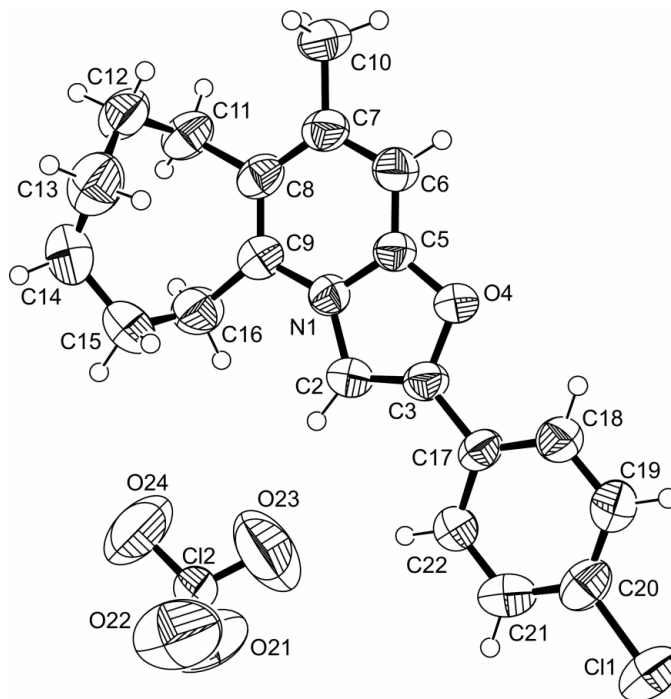


Figure 1 ORTEP-3 (Farrugia, 1997) plot of the title compound and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

H atoms bonded to C atoms were included in calculated positions and refined as riding atoms. Calculated C–H bond lengths are in the range 0.93–0.97 Å. For methyl H atoms, *U*_{iso} values were set equal to 1.5*U*_{eq} of the carrier atoms; for other H atoms, *U*_{iso} values were set to 1.2*U*_{eq} of the carrier atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

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