Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

7-(4-Methylphenyl)cyclopenta[*a*]-quinolizine-10-carbaldehyde

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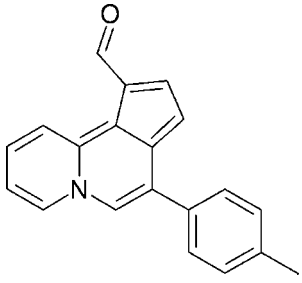
Received 1 October 2010; accepted 19 October 2010

Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.001 Å; R factor = 0.024; wR factor = 0.056; data-to-parameter ratio = 14.5.

In the title compound, $C_{20}H_{15}NO$, the heterotricycle is essential planar [maximum deviation = 0.0790 (5) Å] and makes a dihedral angle of 50.70 (2)° with the benzene ring. The formyl group is almost coplanar with the tricyclic ring, the C C C O torsion angle being −0.78 (13)°.

Related literature

For background to the Vilsmeier Haack reaction, see: Laue & Plagens (2005). For a related structure, see: Borisenko *et al.* (1996).



Experimental

Crystal data

$C_{20}H_{15}NO$ M_r = 285.33
Triclinic, $P\overline{1}$
a = 7.2907 (13) Å
b = 8.9627 (14) Å
c = 12.0162 (19) Å
α = 88.48 (2)°
β = 81.400 (19)°
γ = 67.821 (18)°
V = 718.5 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.64 mm^{-1}
T = 295 K
0.15 × 0.13 × 0.11 mm

Data collection

Enraf Nonius CAD-4 diffractometer
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
T_{min} = 0.649, T_{max} = 1.000
3186 measured reflections
2909 independent reflections
2394 reflections with $I > 2\sigma(I)$
R_{int} = 0.000 **please give correct value**
1 standard reflections every 60 min
intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.056
S = 0.96
2909 reflections
200 parameters
61 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.08 e Å^{-3}
$\Delta\rho_{min}$ = −0.10 e Å^{-3}

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, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP 3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to the Russian Foundation for Basic Research for covering the licence fee for use of the Cambridge Structural Database (Allen, 2002).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2411).

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supplementary materials

Acta Cryst. (2010). E**66**, o2958 [**doi:10.1107/S1600536810042467**]

7-(4-Methylphenyl)cyclopenta[*a*]quinolizine-10-carbaldehyde

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Comment

Cyclopenta[*a*]quinolizines are a novel subclass of non-benzenoid heterocycles π-isoelectronic with azulene, so called pseudoazulenes. Some pseudoazulenes show ambident reactivity towards electrophiles, since both α-sites of the cyclopentadiene ring can be substituted. The Vilsmeier–Haack reaction (Laue & Plagens, 2005) (Fig. 1) was one of the simplest tests to estimate the reactivity of cyclopenta[*a*]quinolizines and the regioselectivity of substitution.

We found that only one product was formed in the reaction. Simple ^{1}H NMR spectra cannot provide an unambiguous proof of the site of substitution. By *X*-ray analysis we proved that the product is the title compound. From this viewpoint it becomes evident, that the strong shift of the proton H-4 signal (10.53 p.p.m. in **1** against 8.16 in the initial compound **2**; Fig. 1) observed in ^{1}H NMR spectra is caused by the *peri*-effect of the formyl group at C7.

In the title compound **1** (Fig. 2), the bond lengths in the heterocyclic core show slight alternations. The bond length between C7 and C71 of the carbonyl group (1.4351 (8) Å) is much shorter than that in the structure of the simplest aromatic ketone, benzaldehyde (1.477 (3) Å; Borisenko *et al.*, 1996). Since the formyl group is almost co-planar with the tricyclic ring (the torsion angle C8—C7—C71═O71 is -0.78 (13)°), it may indicate strong conjugation of the carbonyl group with the π-excessive cyclopentadiene ring.

Experimental

Freshly distilled DMF (1 ml) was added at 263 K to the solution of $POCl_3$ (2.34 mmol, 357 mg) in dry THF (15 ml) forming the Vilsmeier reagent. The solution of 7-(4-methylphenyl)cyclopenta[*a*]quinolizine **2** (300 mg, 1.17 mmol) in dry THF (10 ml) was added dropwise at 273 K to the Vilsmeier reagent. The mixture was stirred overnight at room temperature, diluted with water, and neutralized by NaOH to pH≃ 8. The resultant precipitate was filtered off and recrystallized from DMF. Yield of **1**: 311 mg (93%), m.p. = 527–528 K.

^{1}H NMR (400 MHz; $CDCl_3$; δ, p.p.m.; J, Hz): 2.47 (s, 3H, CH_3), 6.80 (d, J = 4.0, 1H), 7.12 (m, 1H), 7.35 (m, 2H, *Ar*H), 7.61 (m, 2H, *Ar*H), 7.64 (s, 1H), 7.77 (d, J = 4.0, 1H), 7.82 (s, 1H), 8.21 (d, J = 7.1, 1H, H4), 9.92 (s, 1H, CHO), 10.53 (d, J = 7.1, 1H, H1).

Refinement

C-bound H-atoms were placed in calculated positions (C—H 0.93Å; 0.96 Å) and refined as riding, with U_{iso}(H) = 1.2(1.5)U_{eq}(C). The initial experimental data were measured for a full sphere, but at the final stage of the refinement, the 'MERG 2' instruction was used in *SHELXL* and the *DIFABS* procedure (Walker & Stuart, 1983) was applied. As a result, we have FVAR = 1, R_{int} = 0, and the experimental data were reduced to a half-sphere with indices $-8 \le h \le +8$, $-10 \le k \le +11$ and $0 \le l \le +15$.

Figures

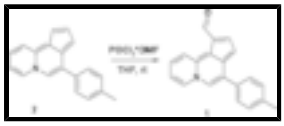


Fig. 1. Synthesis of the title compound.

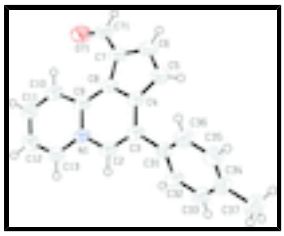


Fig. 2. *ORTEP*-3 plot of the molecular structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

7-(4-Methylphenyl)cyclopenta[*a*]quinolizine-10-carbaldehyde

Crystal data

$C_{20}H_{15}NO$	Z 2
M_r 285.33	$F(000)$ 300
Triclinic, $P\overline{1}$	D_x 1.319 Mg m ^{3}
Hall symbol: P 1	Melting point 527 528 K
a 7.2907 (13) Å	Cu $K\alpha$ radiation, λ 1.54184 Å
b 8.9627 (14) Å	Cell parameters from 25 reflections
c 12.0162 (19) Å	θ 32.0 34.9°
α 88.48 (2)°	μ 0.64 mm ^{1}
β 81.400 (19)°	T 295 K
γ 67.821 (18)°	Prism, pale yellow
V 718.5 (2) Å^3	0.15 × 0.13 × 0.11 mm

Data collection

Enraf Nonius CAD 4 diffractometer	2394 reflections with $I > 2\sigma(I)$
Radiation source: fine focus sealed tube	R_{int} 0.0000
graphite	θ_{max} 75.2°, θ_{min} 3.7°
non profiled ω scans	h 8→9
Absorption correction: part of the refinement model (ΔF) (Walker & Stuart, 1983)	k 10→11
T_{min} 0.649, T_{max} 1.000	l 11→15
3186 measured reflections	1 standard reflections every 60 min
2909 independent reflections	intensity decay: 5%

Refinement

Refinement on F^2	Primary atom site location: structure invariant direct methods
Least squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)]$ 0.024	Hydrogen site location: inferred from neighbouring sites
$wR(F^2)$ 0.056	H atom parameters constrained
S 0.96	w $1/[\sigma^2(F_o^2) + (0.0398P)^2]$ where P $(F_o^2 + 2F_c^2)/3$
2909 reflections	$(\Delta/\sigma)_{max}$ 0.001
200 parameters	$\Delta\rho_{max}$ 0.08 e Å ^{3}
61 restraints	$\Delta\rho_{min}$ 0.10 e Å ^{3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R factor wR and goodness of fit S are based on F^2, conventional R factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
N1	0.20346 (7)	0.58547 (5)	0.01802 (3)	0.05065 (12)
C2	0.09520 (9)	0.71381 (6)	0.09351 (4)	0.05806 (16)
H2	0.0799	0.8176	0.0716	0.070*
C3	0.01070 (9)	0.69255 (6)	0.19859 (4)	0.05301 (14)
C31	0.11306 (9)	0.83714 (6)	0.27192 (4)	0.05427 (14)
C32	0.25884 (9)	0.96616 (6)	0.22956 (5)	0.06118 (16)
H32	0.2771	0.9621	0.1549	0.073*
C33	0.37705 (9)	1.10046 (6)	0.29708 (5)	0.06566 (17)
H33	0.4751	1.1849	0.2674	0.079*
C34	0.35215 (9)	1.11184 (7)	0.40883 (5)	0.06390 (17)
C35	0.20805 (10)	0.98237 (7)	0.45021 (5)	0.06909 (18)
H35	0.1897	0.9867	0.5248	0.083*
C36	0.08989 (9)	0.84623 (7)	0.38403 (4)	0.06206 (16)
H36	0.0053	0.7606	0.4146	0.074*
C37	0.47854 (12)	1.25985 (8)	0.48145 (6)	0.0930 (3)
H37A	0.4965	1.2300	0.5584	0.140*
H37B	0.6068	1.3088	0.4568	0.140*
H37C	0.4128	1.3352	0.4755	0.140*
C4	0.03745 (9)	0.53309 (6)	0.23109 (4)	0.05122 (14)
C5	0.03475 (10)	0.47207 (7)	0.33034 (5)	0.06394 (17)
H5	0.1069	0.5315	0.3957	0.077*
C6	0.02069 (10)	0.30912 (7)	0.31294 (5)	0.06486 (17)
H6	0.0075	0.2406	0.3662	0.078*
C7	0.12585 (9)	0.25977 (6)	0.20378 (4)	0.05555 (15)

C71	0.17458 (10)	0.09745 (6)	0.16468 (5)	0.06569 (17)
H71	0.1522	0.0286	0.2196	0.079*
O71	0.24109 (8)	0.03569 (5)	0.07002 (4)	0.08139 (15)
C8	0.13764 (8)	0.40156 (6)	0.15092 (4)	0.05205 (14)
C9	0.23175 (8)	0.42748 (5)	0.04415 (4)	0.04982 (14)
C10	0.35065 (9)	0.30555 (6)	0.03740 (4)	0.05922 (16)
H10	0.3721	0.1986	0.0218	0.071*
C11	0.43433 (9)	0.34090 (7)	0.13810 (5)	0.06062 (16)
H11	0.5140	0.2589	0.1903	0.073*
C12	0.39948 (9)	0.50275 (7)	0.16278 (5)	0.06187 (16)
H12	0.4525	0.5283	0.2326	0.074*
C13	0.28977 (9)	0.62042 (7)	0.08572 (4)	0.05829 (16)
H13	0.2711	0.7268	0.1018	0.070*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0615 (3)	0.03132 (19)	0.0522 (2)	0.01155 (18)	0.00431 (18)	0.00552 (15)
C2	0.0769 (4)	0.0302 (2)	0.0558 (3)	0.0096 (2)	0.0049 (2)	0.00297 (18)
C3	0.0637 (4)	0.0335 (2)	0.0543 (3)	0.0101 (2)	0.0086 (2)	0.00249 (18)
C31	0.0664 (4)	0.0342 (2)	0.0574 (3)	0.0167 (2)	0.0006 (2)	0.00026 (19)
C32	0.0758 (4)	0.0377 (2)	0.0636 (3)	0.0150 (2)	0.0081 (3)	0.0018 (2)
C33	0.0694 (4)	0.0375 (3)	0.0808 (3)	0.0125 (2)	0.0032 (3)	0.0015 (2)
C34	0.0673 (4)	0.0436 (3)	0.0761 (3)	0.0236 (3)	0.0126 (3)	0.0100 (2)
C35	0.0923 (5)	0.0540 (3)	0.0574 (3)	0.0280 (3)	0.0017 (3)	0.0071 (2)
C36	0.0737 (4)	0.0468 (3)	0.0595 (3)	0.0159 (3)	0.0095 (3)	0.0008 (2)
C37	0.1015 (6)	0.0583 (4)	0.1010 (5)	0.0230 (4)	0.0258 (4)	0.0257 (3)
C4	0.0603 (3)	0.0355 (2)	0.0534 (2)	0.0133 (2)	0.0083 (2)	0.00462 (18)
C5	0.0812 (4)	0.0469 (3)	0.0529 (3)	0.0149 (3)	0.0034 (2)	0.0080 (2)
C6	0.0814 (4)	0.0456 (3)	0.0606 (3)	0.0183 (3)	0.0076 (3)	0.0167 (2)
C7	0.0665 (4)	0.0346 (2)	0.0603 (3)	0.0136 (2)	0.0102 (2)	0.01082 (19)
C71	0.0786 (4)	0.0343 (2)	0.0753 (3)	0.0135 (2)	0.0078 (3)	0.0114 (2)
O71	0.1109 (4)	0.0401 (2)	0.0856 (3)	0.0254 (2)	0.0002 (3)	0.00102 (19)
C8	0.0609 (3)	0.0335 (2)	0.0536 (2)	0.0094 (2)	0.0077 (2)	0.00764 (18)
C9	0.0600 (3)	0.0315 (2)	0.0536 (2)	0.0124 (2)	0.0089 (2)	0.00413 (18)
C10	0.0743 (4)	0.0354 (2)	0.0592 (3)	0.0124 (2)	0.0055 (2)	0.0013 (2)
C11	0.0644 (4)	0.0505 (3)	0.0600 (3)	0.0159 (3)	0.0026 (2)	0.0062 (2)
C12	0.0715 (4)	0.0561 (3)	0.0520 (3)	0.0203 (3)	0.0017 (2)	0.0028 (2)
C13	0.0727 (4)	0.0431 (3)	0.0548 (3)	0.0195 (2)	0.0045 (2)	0.0091 (2)

Geometric parameters (Å, °)

N1	C9	1.3862 (7)	C37	H37C	0.9600
N1	C2	1.3873 (7)	C4	C5	1.4119 (8)
N1	C13	1.3934 (7)	C4	C8	1.4321 (7)
C2	C3	1.3614 (8)	C5	C6	1.3731 (8)
C2	H2	0.9300	C5	H5	0.9300
C3	C4	1.4198 (7)	C6	C7	1.4064 (8)
C3	C31	1.4865 (8)	C6	H6	0.9300

C31 C32	1.3887 (8)	C7 C8	1.4315 (8)
C31 C36	1.3909 (8)	C7 C71	1.4351 (8)
C32 C33	1.3818 (8)	C71 O71	1.2252 (7)
C32 H32	0.9300	C71 H71	0.9300
C33 C34	1.3930 (9)	C8 C9	1.4185 (8)
C33 H33	0.9300	C9 C10	1.4119 (7)
C34 C35	1.3794 (9)	C10 C11	1.3570 (8)
C34 C37	1.5061 (8)	C10 H10	0.9300
C35 C36	1.3843 (8)	C11 C12	1.4065 (9)
C35 H35	0.9300	C11 H11	0.9300
C36 H36	0.9300	C12 C13	1.3428 (8)
C37 H37A	0.9600	C12 H12	0.9300
C37 H37B	0.9600	C13 H13	0.9300
C9 N1 C2	122.34 (5)	C5 C4 C3	132.01 (5)
C9 N1 C13	120.37 (5)	C5 C4 C8	107.93 (5)
C2 N1 C13	117.25 (5)	C3 C4 C8	119.75 (5)
C3 C2 N1	122.08 (5)	C6 C5 C4	107.68 (5)
C3 C2 H2	119.0	C6 C5 H5	126.2
N1 C2 H2	119.0	C4 C5 H5	126.2
C2 C3 C4	118.24 (5)	C5 C6 C7	110.93 (6)
C2 C3 C31	118.72 (5)	C5 C6 H6	124.5
C4 C3 C31	122.97 (5)	C7 C6 H6	124.5
C32 C31 C36	118.33 (5)	C6 C7 C8	106.27 (5)
C32 C31 C3	120.04 (5)	C6 C7 C71	119.19 (6)
C36 C31 C3	121.61 (5)	C8 C7 C71	134.02 (5)
C33 C32 C31	120.75 (6)	O71 C71 C7	129.90 (6)
C33 C32 H32	119.6	O71 C71 H71	115.1
C31 C32 H32	119.6	C7 C71 H71	115.1
C32 C33 C34	121.27 (6)	C9 C8 C7	132.70 (5)
C32 C33 H33	119.4	C9 C8 C4	120.05 (5)
C34 C33 H33	119.4	C7 C8 C4	107.18 (5)
C35 C34 C33	117.44 (5)	N1 C9 C10	117.65 (5)
C35 C34 C37	121.47 (6)	N1 C9 C8	117.11 (5)
C33 C34 C37	121.09 (6)	C10 C9 C8	125.24 (5)
C34 C35 C36	122.00 (6)	C11 C10 C9	121.49 (5)
C34 C35 H35	119.0	C11 C10 H10	119.3
C36 C35 H35	119.0	C9 C10 H10	119.3
C35 C36 C31	120.20 (6)	C10 C11 C12	119.40 (5)
C35 C36 H36	119.9	C10 C11 H11	120.3
C31 C36 H36	119.9	C12 C11 H11	120.3
C34 C37 H37A	109.5	C13 C12 C11	120.09 (5)
C34 C37 H37B	109.5	C13 C12 H12	120.0
H37A C37 H37B	109.5	C11 C12 H12	120.0
C34 C37 H37C	109.5	C12 C13 N1	120.95 (5)
H37A C37 H37C	109.5	C12 C13 H13	119.5
H37B C37 H37C	109.5	N1 C13 H13	119.5
C9 N1 C2 C3	0.42 (9)	C5 C6 C7 C71	172.26 (6)
C13 N1 C2 C3	177.64 (5)	C6 C7 C71 O71	169.69 (7)

N1 C2 C3 C4	0.70 (9)	C8 C7 C71 O71	0.78 (13)
N1 C2 C3 C31	176.42 (5)	C6 C7 C8 C9	176.75 (6)
C2 C3 C31 C32	47.59 (9)	C71 C7 C8 C9	11.90 (12)
C4 C3 C31 C32	129.39 (7)	C6 C7 C8 C4	0.13 (7)
C2 C3 C31 C36	133.71 (7)	C71 C7 C8 C4	171.22 (7)
C4 C3 C31 C36	49.31 (9)	C5 C4 C8 C9	177.74 (5)
C36 C31 C32 C33	0.33 (10)	C3 C4 C8 C9	7.92 (9)
C3 C31 C32 C33	179.07 (5)	C5 C4 C8 C7	0.38 (7)
C31 C32 C33 C34	0.92 (10)	C3 C4 C8 C7	174.73 (6)
C32 C33 C34 C35	1.43 (10)	C2 N1 C9 C10	177.72 (5)
C32 C33 C34 C37	178.76 (6)	C13 N1 C9 C10	0.29 (8)
C33 C34 C35 C36	0.72 (10)	C2 N1 C9 C8	2.57 (8)
C37 C34 C35 C36	179.47 (6)	C13 N1 C9 C8	179.42 (5)
C34 C35 C36 C31	0.51 (10)	C7 C8 C9 N1	176.80 (6)
C32 C31 C36 C35	1.03 (9)	C4 C8 C9 N1	6.65 (8)
C3 C31 C36 C35	179.75 (6)	C7 C8 C9 C10	2.89 (11)
C2 C3 C4 C5	177.57 (6)	C4 C8 C9 C10	173.67 (5)
C31 C3 C4 C5	0.58 (11)	N1 C9 C10 C11	0.16 (9)
C2 C3 C4 C8	4.81 (9)	C8 C9 C10 C11	179.52 (5)
C31 C3 C4 C8	172.18 (5)	C9 C10 C11 C12	1.05 (10)
C3 C4 C5 C6	174.15 (7)	C10 C11 C12 C13	2.19 (10)
C8 C4 C5 C6	0.76 (7)	C11 C12 C13 N1	2.10 (10)
C4 C5 C6 C7	0.87 (8)	C9 N1 C13 C12	0.86 (9)
C5 C6 C7 C8	0.62 (7)	C2 N1 C13 C12	178.96 (5)

Fig. 1

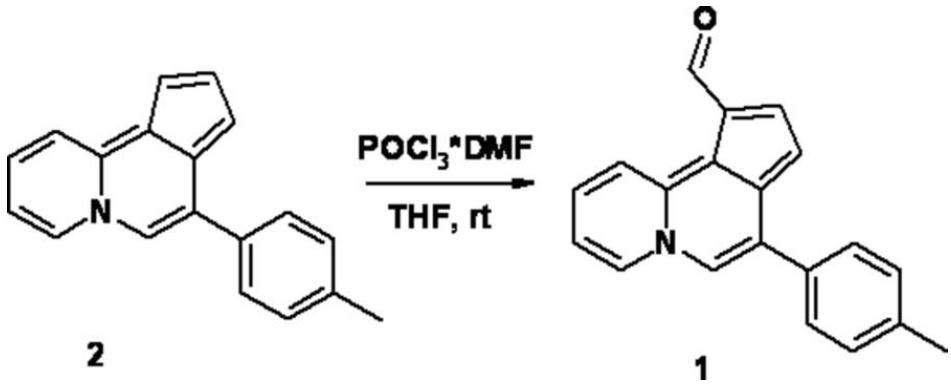
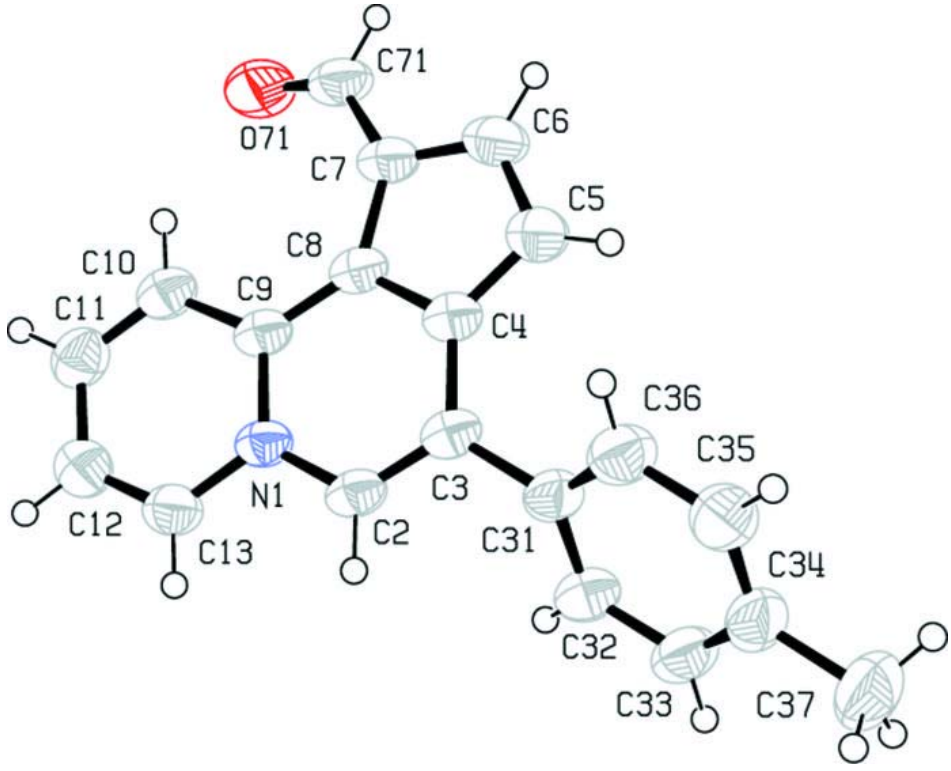


Fig. 2


C71
O71
C6
C7
C5
C8
C10
C9
C11
C4
C36
C35
N1
C3
C12
C2
C31
C13
C34
C32
C33
C37