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1-Methyl-5-(3-nitrophenyl)-3-oxocyclohexanecarbonitrile

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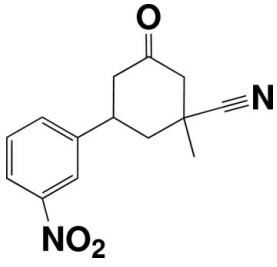
Key indicators: single-crystal X-ray study; T = 160 K; mean σ(C–C) = 0.002 Å; R factor = 0.056; wR factor = 0.163; data-to-parameter ratio = 17.1.

In the title molecule, $C_{14}H_{14}N_2O_3$, the cyclohexane ring adopts a chair conformation. The cyano group and methyl groups have axial and equatorial orientations, respectively. The benzene ring has an equatorial orientation. In the crystal structure, the molecules are stabilized by intermolecular C—H···N hydrogen bonds.

Related literature

For related literature, see: Nagata *et al.* (1961); Pandey *et al.* (2004).



Experimental

Crystal data

$C_{14}H_{14}N_2O_3$
M_r = 258.27
Monoclinic, $P2_1/a$
a = 12.2284 (3) Å
b = 8.0986 (3) Å
c = 13.1376 (4) Å
β = 91.336 (2)°
V = 1300.70 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 160 (2) K
0.25 × 0.2 × 0.13 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
32792 measured reflections
2968 independent reflections
2055 reflections with $I > 2\sigma(I)$
R_{int} = 0.097

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.163
S = 1.05
2968 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···N311^{i}	0.99	2.50	3.470 (2)	167

Symmetry code: (i) $-x, -y+1, -z+1$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

The data collection was carried out by Dr A. Linden of the Institute of Organic Chemistry at the University of Zurich. The help is gratefully acknowledged by AT.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2280).

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supplementary materials

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1-Methyl-5-(3-nitrophenyl)-3-oxocyclohexanecarbonitrile

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Comment

Related literature were reported by Nagata *et al.*, 1961 and Pandey *et al.*, 2004.

The present X-ray diffraction study was undertaken to determine how the conformation of the system is affected by the substitution of a cyano and methyl groups at position 3 and *m*-nitrophenyl ring at position 5 of the cyclohexanone. The molecular structure of (I), with atomic numbering scheme is shown in Fig. 1. The cyclohexane ring adopts a chair conformation. The cyano group and the methyl group at position 3 have an axial and equatorial orientations respectively. The phenyl ring at position 5 has an equatorial orientation. The mean plane of atoms C2/C3/C5/C6 and phenyl ring make dihedral angle of 75.97 (6)°. The attached *m*-nitro group make a 2.4 (3)° tilt with the phenyl ring. In the crystal structure the molecules are stabilized by intermolecular C2–H2B···N311 hydogen bonds (Fig. 2).

Experimental

A mixture of 3-methyl-5-*m*-nitrophenylcyclohex-2-enone (4.62 g, 0.02 mol), potassium cyanide (2.6 g, 0.04 mol), ammonium chloride (1.59 g, 0.03 mol), dimethyl formamide (50 ml) and water (2 ml) was heated with stirring for 16-18 h at 353 K. The reaction mixture was cooled to room temperature and poured into water. The product was extracted with CH_2Cl_2 (3x10 ml) and the organic layer was dried, evaporated and purified by column chromatography (hexane-EtOAc, 4.5:1 v/v). The yield of the isolated product was 3.87 g (75%).

Refinement

H atoms were positioned geometrically and allowed to ride on their parent atoms, with C–H = 0.95-0.99 Å and U_{iso}=1.2 or 1.5 times U_{eq}(C).

Figures

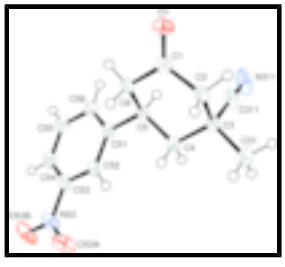

Fig. 1. The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

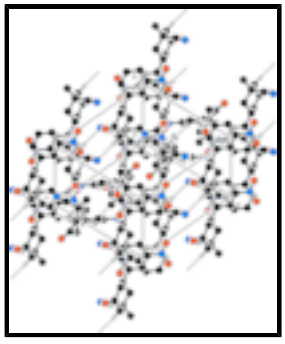

Fig. 2. The molecular packing of (I), viewed down the b axis. Dashed lines indicate hydrogen bonds.

1-Methyl-5-(3-nitrophenyl)-3-oxocyclohexanecarbonitrile

Crystal data

$C_{14}H_{14}N_2O_3$	F_{000} = 544
M_r = 258.27	D_x = 1.319 Mg m^{-3}
Monoclinic, $P2_1/a$	Melting point: 387 K
Hall symbol: -P 2 y a b	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 12.2284 (3) Å	Cell parameters from 3165 reflections
b = 8.0986 (3) Å	θ = 2–27.5º
c = 13.1376 (4) Å	μ = 0.09 mm^{-1}
β = 91.336 (2)º	T = 160 (2) K
V = 1300.70 (7) Å^3	Plate, orange
Z = 4	0.25 × 0.2 × 0.13 mm

Data collection

Nonius KappaCCD area-detector diffractometer	2968 independent reflections
Radiation source: Nonius FR590 sealed tube generator	2055 reflections with $I > 2\sigma(I)$
Monochromator: horizontally mounted graphite crystal	R_{int} = 0.097
Detector resolution: 9 pixels mm^{-1}	θ_{max} = 27.5º
T = 160(1) K	θ_{min} = 3.0º
φ and ω scans with κ offsets	h = −15→15
Absorption correction: none	k = −10→10
32792 measured reflections	l = −17→17

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2 + 0.0906P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.056	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.163	$\Delta\rho_{max}$ = 0.35 e Å^{-3}

S = 1.05	$\Delta\rho_{min}$ = −0.29 e Å^{-3}
2968 reflections	Extinction correction: SHELXL97, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
174 parameters	Extinction coefficient: 0.060 (7)
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Experimental. Solvent used: Cooling Device: Oxford Cryosystems Cryostream 700 Crystal mount: glued on a glass fibre Mosaicity (deg.): 0.485 (2) Frames collected: 341 Seconds exposure per frame: 30 Degrees rotation per frame: 2.0 Crystal-Detector distance (mm): 30.0

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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 $F^2 > 2\text{sigma}(F^2)$ 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}
O1	0.12273 (10)	0.92625 (17)	0.54801 (9)	0.0339 (4)
O53A	0.24351 (12)	1.0799 (2)	−0.04547 (11)	0.0502 (6)
O53B	0.14631 (12)	1.2738 (2)	−0.11608 (11)	0.0540 (6)
N53	0.16554 (13)	1.1753 (2)	−0.04660 (12)	0.0376 (6)
N311	−0.09375 (13)	0.5722 (2)	0.38559 (16)	0.0515 (7)
C1	0.13526 (12)	0.8854 (2)	0.45983 (13)	0.0249 (5)
C2	0.16985 (13)	0.7131 (2)	0.43218 (13)	0.0256 (5)
C3	0.10791 (12)	0.6410 (2)	0.33822 (13)	0.0239 (5)
C4	0.10443 (13)	0.7681 (2)	0.25184 (13)	0.0243 (5)
C5	0.05352 (12)	0.9313 (2)	0.28443 (12)	0.0217 (5)
C6	0.12067 (13)	1.0061 (2)	0.37311 (13)	0.0250 (5)
C31	0.16269 (16)	0.4811 (2)	0.30333 (16)	0.0358 (6)
C51	0.03902 (13)	1.0541 (2)	0.19846 (12)	0.0229 (5)
C52	0.10960 (13)	1.0585 (2)	0.11632 (13)	0.0249 (5)
C53	0.09084 (14)	1.1732 (2)	0.03957 (13)	0.0279 (5)
C54	0.00549 (15)	1.2825 (2)	0.03984 (14)	0.0332 (6)
C55	−0.06329 (15)	1.2804 (2)	0.12226 (15)	0.0349 (6)
C56	−0.04613 (14)	1.1673 (2)	0.20033 (14)	0.0295 (6)
C311	−0.00532 (14)	0.6019 (2)	0.36614 (15)	0.0317 (6)
H2A	0.24915	0.71362	0.41861	0.0307*
H2B	0.15819	0.63968	0.49119	0.0307*

H4A	0.06158	0.72249	0.19347	0.0291*
H4B	0.17978	0.78864	0.22894	0.0291*
H5	−0.02087	0.90594	0.31033	0.0260*
H6A	0.08331	1.10626	0.39788	0.0299*
H6B	0.19339	1.03937	0.34867	0.0299*
H31A	0.12151	0.43534	0.24499	0.0537*
H31B	0.23782	0.50483	0.28344	0.0537*
H31C	0.16376	0.40101	0.35925	0.0537*
H52	0.16946	0.98404	0.11315	0.0298*
H54	−0.00627	1.35768	−0.01485	0.0398*
H55	−0.12224	1.35656	0.12528	0.0419*
H56	−0.09380	1.16735	0.25641	0.0353*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0349 (7)	0.0451 (9)	0.0217 (7)	−0.0008 (6)	−0.0007 (5)	−0.0026 (6)
O53A	0.0420 (8)	0.0731 (12)	0.0360 (9)	0.0045 (8)	0.0105 (6)	0.0136 (8)
O53B	0.0546 (9)	0.0728 (12)	0.0347 (9)	−0.0096 (8)	0.0010 (7)	0.0312 (8)
N53	0.0368 (9)	0.0501 (11)	0.0257 (9)	−0.0121 (8)	−0.0013 (7)	0.0094 (8)
N311	0.0284 (9)	0.0470 (12)	0.0791 (14)	−0.0042 (8)	0.0007 (8)	0.0296 (10)
C1	0.0182 (8)	0.0315 (10)	0.0249 (10)	−0.0048 (7)	−0.0028 (6)	0.0012 (8)
C2	0.0257 (9)	0.0268 (10)	0.0241 (9)	0.0003 (7)	−0.0023 (7)	0.0063 (7)
C3	0.0203 (8)	0.0224 (9)	0.0290 (10)	−0.0018 (7)	−0.0007 (7)	0.0043 (7)
C4	0.0248 (9)	0.0248 (10)	0.0232 (9)	−0.0004 (7)	−0.0002 (7)	0.0025 (7)
C5	0.0193 (8)	0.0225 (9)	0.0234 (9)	−0.0009 (6)	0.0026 (6)	0.0036 (7)
C6	0.0270 (9)	0.0227 (10)	0.0252 (9)	−0.0017 (7)	0.0006 (7)	0.0011 (7)
C31	0.0365 (10)	0.0266 (10)	0.0440 (12)	0.0046 (8)	−0.0059 (8)	−0.0010 (9)
C51	0.0234 (8)	0.0226 (9)	0.0226 (9)	−0.0039 (7)	−0.0030 (7)	0.0025 (7)
C52	0.0231 (9)	0.0265 (10)	0.0249 (9)	−0.0041 (7)	−0.0021 (7)	0.0039 (7)
C53	0.0309 (9)	0.0309 (10)	0.0218 (9)	−0.0104 (8)	−0.0029 (7)	0.0046 (8)
C54	0.0417 (11)	0.0281 (10)	0.0292 (10)	−0.0055 (8)	−0.0092 (8)	0.0065 (8)
C55	0.0374 (10)	0.0306 (11)	0.0365 (11)	0.0061 (8)	−0.0058 (8)	0.0057 (8)
C56	0.0279 (9)	0.0299 (10)	0.0306 (10)	0.0012 (8)	0.0014 (7)	0.0022 (8)
C311	0.0275 (10)	0.0263 (10)	0.0410 (11)	−0.0012 (8)	−0.0049 (8)	0.0112 (8)

Geometric parameters (Å, °)

O1—C1	1.218 (2)	C53—C54	1.369 (2)
O53A—N53	1.227 (2)	C54—C55	1.387 (3)
O53B—N53	1.231 (2)	C55—C56	1.387 (3)
N53—C53	1.471 (2)	C2—H2A	0.9900
N311—C311	1.143 (2)	C2—H2B	0.9900
C1—C2	1.505 (2)	C4—H4A	0.9900
C1—C6	1.509 (2)	C4—H4B	0.9900
C2—C3	1.548 (2)	C5—H5	1.0000
C3—C4	1.532 (2)	C6—H6A	0.9900
C3—C31	1.533 (2)	C6—H6B	0.9900
C3—C311	1.475 (2)	C31—H31A	0.9800

C4—C5	1.527 (2)	C31—H31B	0.9800
C5—C6	1.534 (2)	C31—H31C	0.9800
C5—C51	1.512 (2)	C52—H52	0.9500
C51—C52	1.398 (2)	C54—H54	0.9500
C51—C56	1.388 (2)	C55—H55	0.9500
C52—C53	1.386 (2)	C56—H56	0.9500
O1···C31^{i}	3.265 (2)	H4A···C52	2.9700
O1···C5^{ii}	3.323 (2)	H4A···H31A	2.5300
O1···C6^{ii}	3.221 (2)	H4A···O53B^{v}	2.7200
O53A···C55^{iii}	3.387 (2)	H4A···H54^{v}	2.5100
O1···H2A^{i}	2.8300	H4B···C52	2.7600
O1···H31B^{i}	2.8400	H4B···H6B	2.5700
O1···H5^{ii}	2.6400	H4B···H31B	2.5100
O1···H6A^{ii}	2.6500	H4B···H52	2.2000
O1···H56^{ii}	2.7100	H4B···O53B^{xiii}	2.6200
O1···H31C^{i}	2.8600	H5···C311	2.5700
O53A···H52	2.4200	H5···H56	2.4000
O53A···H55^{iii}	2.8000	H5···O1^{ii}	2.6400
O53B···H54	2.4100	H6A···C56	3.0500
O53B···H4B^{iv}	2.6200	H6A···O1^{ii}	2.6500
O53B···H52^{iv}	2.8200	H6B···H4B	2.5700
O53B···H4A^{v}	2.7200	H6B···N311^{viii}	2.7900
N311···C2^{vi}	3.441 (2)	H31A···C55^{xiv}	3.0200
N311···H2B^{vii}	2.5000	H31A···C56^{xiv}	3.0300
N311···H2A^{vi}	2.6300	H31A···H4A	2.5300
N311···H6B^{vi}	2.7900	H31B···H2A	2.4500
C2···N311^{viii}	3.441 (2)	H31B···H4B	2.5100
C5···O1^{ii}	3.323 (2)	H31B···O1^{ix}	2.8400
C6···O1^{ii}	3.221 (2)	H31B···H56^{viii}	2.5200
C31···O1^{ix}	3.265 (2)	H31C···H2B	2.6000
C55···O53A^{x}	3.387 (2)	H31C···O1^{ix}	2.8600
C4···H52	2.6600	H52···O53A	2.4200
C52···H4A	2.9700	H52···C4	2.6600
C52···H4B	2.7600	H52···H4B	2.2000
C54···H54^{xi}	2.9300	H52···O53B^{xiii}	2.8200
C55···H31A^{xii}	3.0200	H54···O53B	2.4100
C56···H6A	3.0500	H54···C54^{xi}	2.9300
C56···H31A^{xii}	3.0300	H54···H4A^{v}	2.5100
C311···H5	2.5700	H54···H54^{xi}	2.3400
H2A···H31B	2.4500	H55···O53A^{x}	2.8000
H2A···O1^{ix}	2.8300	H56···H5	2.4000
H2A···N311^{viii}	2.6300	H56···O1^{ii}	2.7100

H2B···H31C	2.6000	H56···H31B[vi]	2.5200
H2B···N311[vii]	2.5000		
O53A—N53—O53B	123.51 (16)	C3—C2—H2B	109.00
O53A—N53—C53	118.66 (15)	H2A—C2—H2B	108.00
O53B—N53—C53	117.83 (15)	C3—C4—H4B	109.00
O1—C1—C2	121.58 (15)	C3—C4—H4A	109.00
O1—C1—C6	121.81 (15)	H4A—C4—H4B	108.00
C2—C1—C6	116.58 (14)	C5—C4—H4A	109.00
C1—C2—C3	114.03 (13)	C5—C4—H4B	109.00
C2—C3—C4	110.00 (13)	C51—C5—H5	107.00
C2—C3—C31	110.37 (13)	C4—C5—H5	107.00
C2—C3—C311	109.12 (14)	C6—C5—H5	107.00
C4—C3—C31	110.54 (14)	C1—C6—H6B	109.00
C4—C3—C311	108.57 (13)	C1—C6—H6A	109.00
C31—C3—C311	108.20 (14)	H6A—C6—H6B	108.00
C3—C4—C5	112.24 (14)	C5—C6—H6A	109.00
C4—C5—C6	109.90 (13)	C5—C6—H6B	109.00
C4—C5—C51	113.67 (13)	H31A—C31—H31B	109.00
C6—C5—C51	111.03 (13)	C3—C31—H31A	109.00
C1—C6—C5	111.68 (13)	C3—C31—H31B	109.00
C5—C51—C52	121.98 (14)	C3—C31—H31C	109.00
C5—C51—C56	119.74 (14)	H31A—C31—H31C	109.00
C52—C51—C56	118.28 (15)	H31B—C31—H31C	109.00
C51—C52—C53	118.94 (15)	C51—C52—H52	121.00
N53—C53—C52	118.18 (15)	C53—C52—H52	121.00
N53—C53—C54	118.80 (15)	C55—C54—H54	121.00
C52—C53—C54	123.01 (16)	C53—C54—H54	121.00
C53—C54—C55	118.07 (16)	C56—C55—H55	120.00
C54—C55—C56	120.09 (16)	C54—C55—H55	120.00
C51—C56—C55	121.57 (16)	C51—C56—H56	119.00
C3—C2—H2A	109.00	C55—C56—H56	119.00
C1—C2—H2A	109.00	N311—C311—C3	178.5 (2)
C1—C2—H2B	109.00		
O53A—N53—C53—C52	−2.6 (2)	C4—C5—C6—C1	−53.75 (17)
O53A—N53—C53—C54	178.27 (17)	C51—C5—C6—C1	179.64 (13)
O53B—N53—C53—C52	177.67 (16)	C4—C5—C51—C52	−30.4 (2)
O53B—N53—C53—C54	−1.5 (2)	C4—C5—C51—C56	150.01 (15)
O1—C1—C2—C3	137.96 (15)	C6—C5—C51—C52	94.13 (18)
C6—C1—C2—C3	−44.03 (19)	C6—C5—C51—C56	−85.48 (18)
O1—C1—C6—C5	−134.95 (15)	C5—C51—C52—C53	179.33 (15)
C2—C1—C6—C5	47.06 (18)	C56—C51—C52—C53	−1.1 (2)
C1—C2—C3—C4	46.89 (18)	C5—C51—C56—C55	−179.03 (15)
C1—C2—C3—C31	169.12 (14)	C52—C51—C56—C55	1.4 (3)
C1—C2—C3—C311	−72.11 (17)	C51—C52—C53—N53	−179.61 (15)
C2—C3—C4—C5	−56.14 (16)	C51—C52—C53—C54	−0.5 (3)
C31—C3—C4—C5	−178.28 (13)	N53—C53—C54—C55	−179.16 (15)
C311—C3—C4—C5	63.19 (17)	C52—C53—C54—C55	1.7 (3)
C3—C4—C5—C6	60.31 (17)	C53—C54—C55—C56	−1.4 (3)

C3—C4—C5—C51	−174.57 (13)	C54—C55—C56—C51	−0.1 (3)

Symmetry codes: (i) −*x*+1/2, *y*+1/2, −*z*+1; (ii) −*x*, −*y*+2, −*z*+1; (iii) *x*+1/2, −*y*+5/2, *z*; (iv) −*x*+1/2, *y*+1/2, −*z*; (v) −*x*, −*y*+2, −*z*; (vi) *x*−1/2, −*y*+3/2, *z*; (vii) −*x*, −*y*+1, −*z*+1; (viii) *x*+1/2, −*y*+3/2, *z*; (ix) −*x*+1/2, *y*−1/2, −*z*+1; (x) *x*−1/2, −*y*+5/2, *z*; (xi) −*x*, −*y*+3, −*z*; (xii) *x*, *y*+1, *z*; (xiii) −*x*+1/2, *y*−1/2, −*z*; (xiv) *x*, *y*−1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2B···N311^{vii}	0.99	2.50	3.470 (2)	167

Symmetry codes: (vii) −*x*, −*y*+1, −*z*+1.

Fig. 1

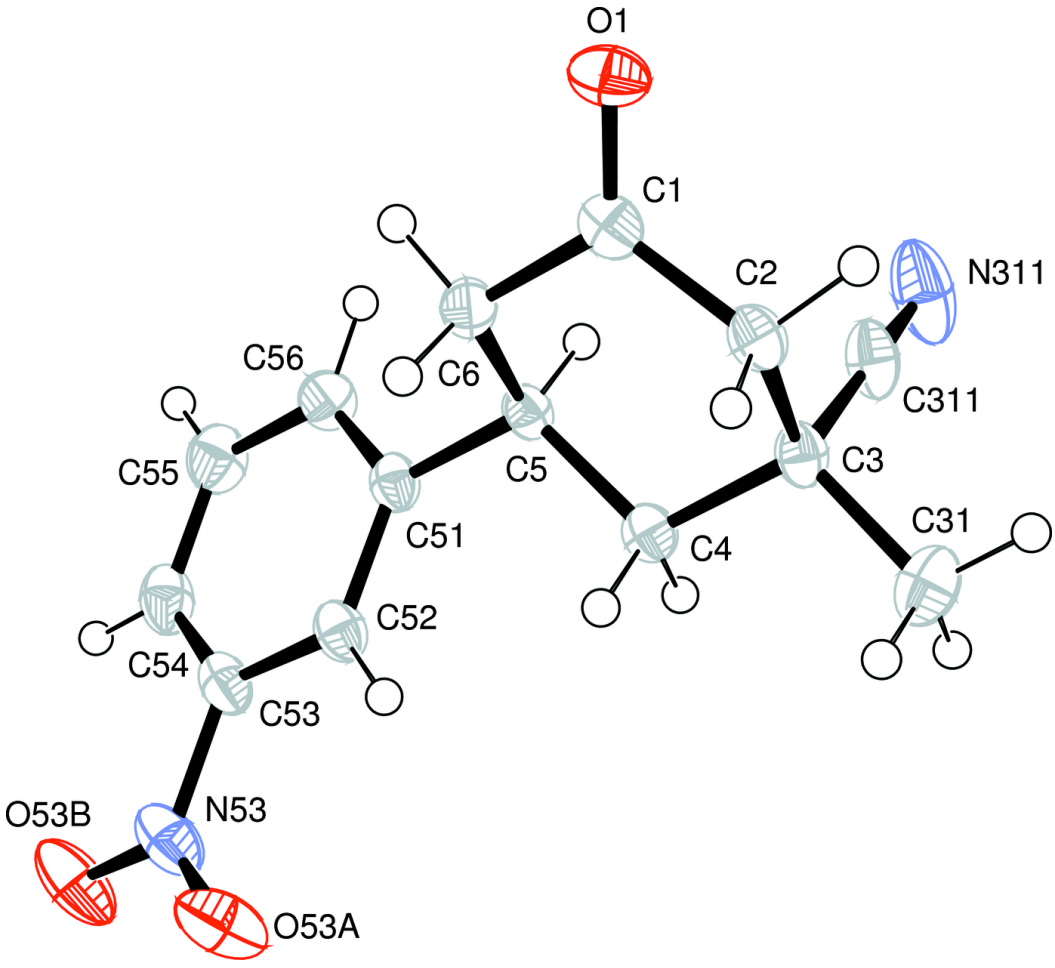
O1
C1
C2
N311
C311
C3
C31
C4
C5
C6
C56
C55
C51
C52
C54
C53
N53
O53B
O53A

Fig. 2