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(*E*)-2-(4-Chlorobenzylidene)cyclooctanone

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Key indicators

Single-crystal X-ray study
T = 288 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.079
Data-to-parameter ratio = 20.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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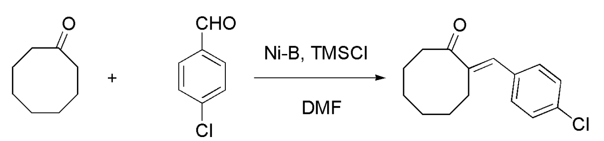
The title compound, $C_{15}H_{17}ClO$, was synthesized directly from the condensation of cyclooctanone with 4-chlorobenzaldehyde, catalysed effectively by improved nanostructured Ni–B cluster in the presence of trimethylsilyl chloride (TMSCl). The eight-membered ring adopts a boat–chair conformation. The packing of the molecules in the crystal structure is determined mainly by C—H$\cdots$O hydrogen bonds, together with C—H$\cdots\pi$ interactions and weak π–π stacking interactions.

Comment

The aldol condensation reaction, which is performed in the presence of strong acids or bases, is one of the most useful reactions in organic chemistry. Ni–B/TMSCl is used as a catalytic system for the aldol condensation reaction, and the title compound, (I), was obtained in excellent yield. The structure of (*E*)-2-(2-fluorobenzylidene)cyclooctanone, (II), has already been reported (Huang *et al.*, 2004). We report here the structure of analog (I).



(I)

Fig. 1 shows the molecular structure of (I), which crystallizes in the space group $P2_1$. The eight-membered ring adopts a boat–chair conformation. In general, cyclooctanone can adopt two conformations, *viz*. crown or boat–chair (Allinger & Greenberg, 1959). The boat–chair conformation is favourable

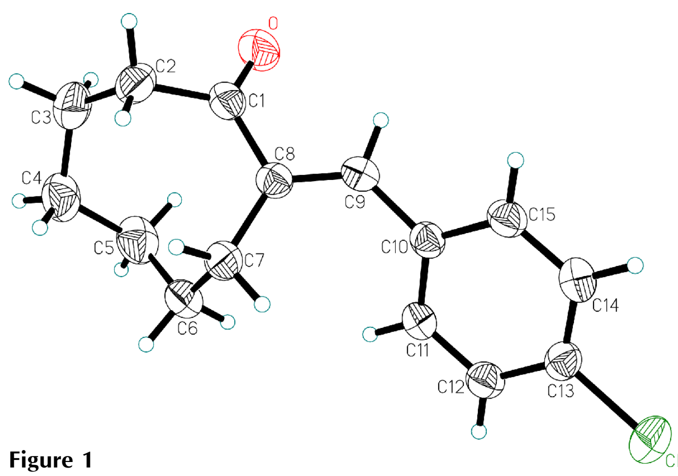


Figure 1
A view of the title compound, (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

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for the cyclooctanone ring of (I), in view of the chlorobenzylidene substituent.

There are no unusual bond lengths and angles in (I), and the geometry is in good agreement with that found in (II). The C1—C8—C9—C10 torsion angle of 179.84 (19)° confirms the *E* configuration of the molecule with respect to the C8=C9 bond. The O—C1—C8—C9 torsion angle of 29.4 (3)°, together with normal C1=O and C8=C9 bond lengths (Table 1) indicate the absence of conjugation between these two double bonds. Also, the C8—C9—C10—C11 torsion angle of 42.4 (3)°, and the dihedral angle between the C8=C9—C10 plane and the benzene ring of 42.5 (1)° show that the C8=C9 bond does not conjugate with the benzene ring.

In the fluoro analog, (II), benzene ring atoms C11 and C14 are hydrogen bonded to the O atom of symmetry-related molecules at $(1-x,\ 1-y,\ z-\frac{1}{2})$ and $(x+\frac{1}{2},\ \frac{3}{2}-y,\ z)$, respectively. In addition, atom C4 is involved in two separate C—H⋯π interactions with the benzene ring of symmetry-related molecules at $(\frac{1}{2}-x, \frac{3}{2}+y, \frac{1}{2}+z)$ and $(x, 1+y, z)$.

The supramolecular structure of (I), however, is completely different. A network of intermolecular C—H⋯O and C—H...π interactions is present (Table 2). In addition, there is a comparatively weak π–π interaction between the benzene ring and a symmetry-related ring at $(1-x, y-\frac{1}{2}, 2-z)$, with their centroids separated by 5.530 (9) Å and a dihedral angle between the two planes of 85.0 (2)%.

Finally, it is worth mentioning that there is a large difference between the melting points of (I) and (II), *viz*. 362–364 and 465–466 K, respectively.

Experimental

A solution of cyclooctanone (1.0 mmol), 4-chlorobenzaldehyde (1.0 mmol) and TMSCl (1.1 mmol) in dimethylformamide (DMF, 1 ml) with 2 mol% of improved nanostructured Ni–B cluster was heated at 348 K for 5 h. A crystalline product precipitated directly when the whole reaction mixture was placed in a refrigerator overnight. This was isolated by filtration, washed with ethanol, and dried (yield 85%). The crystalline product was dissolved in a DMF/methanol solution. Single crystals (m.p. 362–364 K) suitable for X-ray structure analysis were obtained by slow evaporation of the solution at room temperature.

Crystal data

$C_{15}H_{17}ClO$	D_x = 1.243 Mg m^{-3}
M_r = 248.74	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 34 reflections
a = 7.474 (1) Å	θ = 2.8–15.2°
b = 10.545 (1) Å	μ = 0.27 mm^{-1}
c = 8.568 (1) Å	T = 288 (2) K
β = 100.223 (9)°	Block, colorless
V = 664.6 (1) Å^3	0.48 × 0.40 × 0.38 mm
Z = 2	

Data collection

Siemens *P*4 diffractometer	R_{int} = 0.016
ω scans	θ_{max} = 27.7°
Absorption correction: multi-scan (*SHELXTL*; Siemens, 1991)	h = −9 → 9
T_{min} = 0.858, T_{max} = 0.898	k = −13 → 13
3675 measured reflections	l = −11 → 11
3115 independent reflections	3 standard reflections every 97 reflections
2310 reflections with $I > 2\sigma(I)$	intensity decay: 3.5%

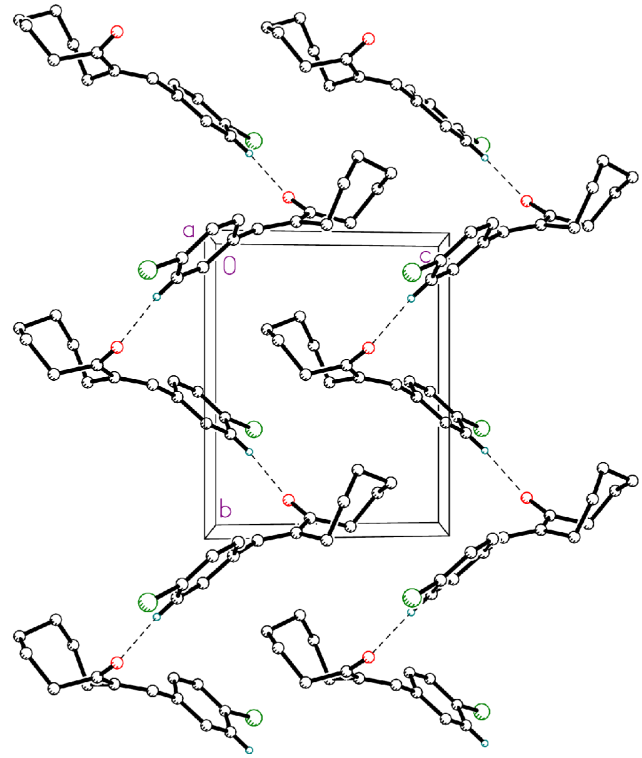

Figure 2
The crystal packing of the title compound, (I), viewed down the *a* axis. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ < 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.036	$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$wR(F^2)$ = 0.079	$\Delta\rho_{min}$ = −0.11 e Å^{-3}
S = 0.96	Extinction correction: *SHELXL*
3115 reflections	Extinction coefficient: 0.056 (4)
155 parameters	Absolute structure: (Flack, 1983); 1473 Friedel pairs
H-atom parameters constrained	Flack parameter = −0.01 (6)
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cl—C13	1.7489 (18)	C8—C9	1.339 (2)
O—C1	1.214 (2)	C9—C10	1.474 (2)
C1—C8	1.494 (3)		
O—C1—C8	121.19 (18)	O—C1—C2	118.48 (18)
C8—C1—C2—C3	−100.7 (2)	C4—C5—C6—C7	−60.5 (3)
C1—C2—C3—C4	71.2 (3)	C5—C6—C7—C8	−49.9 (3)
C2—C3—C4—C5	−62.5 (3)	C2—C1—C8—C7	26.5 (3)
C3—C4—C5—C6	102.7 (3)	C6—C7—C8—C1	73.9 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C14—H14⋯O^{i}	0.93	2.43	3.314 (3)	159
C4—H4B⋯Cg^{ii}	0.97	2.87	3.806 (8)	164
C5—H5A⋯Cg^{iii}	0.97	3.27	4.065 (0)	141

Symmetry codes: (i) $2-x, \frac{1}{2}+y, 2-z$; (ii) $x, y, z-1$; (iii) $1-x, y-\frac{1}{2}, 1-z$. Cg is the centroid of the benzene ring.

H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å, and refined as riding atoms, with $U_{iso}(H) = 1.2U_{eq}$(carrier atom).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL*/*PC* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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References

Allinger, N. L. & Greenberg, S. (1959). *J. Am. Chem. Soc.* **81**, 5733–5736.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Huang, S., Zhu, Y. & Pan, Y. (2004). *Acta Cryst.* E**60**, o1000–o1002.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1991). *SHELXTL/PC*. Version 5.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994). *XSCANS*. Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.