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N-(4-Chlorophenyl)-9*H*-fluoren-9-imine

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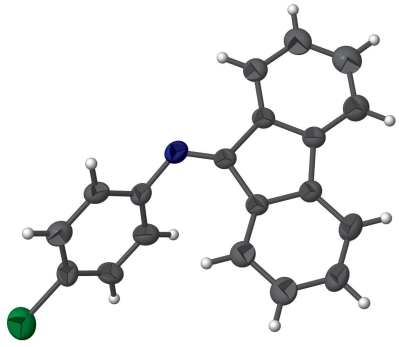
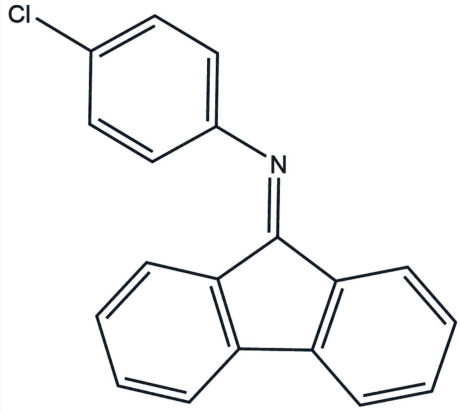
The title compound, $C_{19}H_{12}ClN$, was synthesized *via* reaction of 9-fluorenone and 4-chloroaniline using *p*-toluenesulfonic acid in toluene. The dihedral angle between the fluorene moiety (r.m.s. deviation = 0.027 Å) and the chlorophenyl ring is 64.59 (6)° and a possible weak intramolecular C—H···π interaction occurs.

3D view



Chemical scheme



Structure description

Acid-catalyzed imine formation reactions between 9-fluorenone and anilines are easy, high-yield projects for undergraduate research. Fluoren-9-imines are of interest because of their interesting fluorescence (Dufresne *et al.*, 2011) and use as potential organics in materials with tunable HLG (HOMO–LUMO gap) systems (Eakins *et al.*, 2013). The crystal structure of *N*-phenyl-*9H*-fluoren-9-imine, the stripped-down combination between 9-fluorenone and aniline, has been published three times. The first paper described the structure of a monoclinic benzene solvate (Peters *et al.*, 1998). Unsolvated monoclinic and orthorhombic forms were published by Eakins *et al.* (2013) and Dufresne *et al.* (2011), respectively. Four additional complexes made from 9-fluorenone and substituted anilines have been published: a 4-methylaniline derivate (Bai *et al.*, 2009) and 3,4-dimethylaniline, 2-methoxy aniline and 4-methoxyaniline derivatives (Glagovich *et al.*, 2004*a*,*b*,*c*). Finally, the crystal structure of *N*-mesityl-*9H*-fluoren-9-imine was communicated privately to the CSD in 2016 (Evans *et al.* 2016). As part of our studies in this area, we now describe the synthesis and structure of the title compound.

In the title molecule (Fig. 1), all bond lengths and angles are within expected values: the dihedral angle between the fluorene ring system and the chlorophenyl ring is 64.59 (6)°. A possible weak intramolecular C3—H3···π interaction (Table 1) occurs. In the crystal, the molecules pack in interweaving layers (Fig. 2).

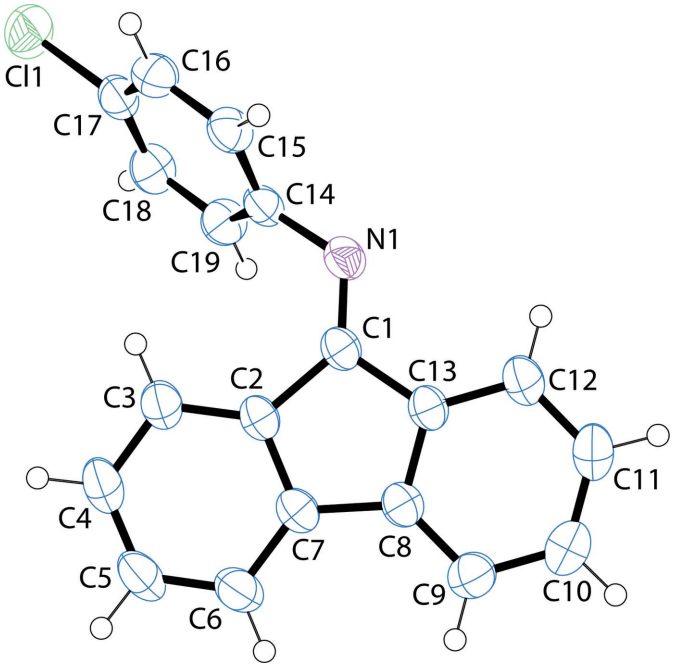


Figure 1
The molecular structure of the title compound showing 50% probability displacement ellipsoids.

Synthesis and crystallization

To a 100 ml round-bottom flask were added 0.326 g (1.81 mmol) of 9-fluorenone, 0.46 g (3.62 mmol) of 4-chloroaniline, 0.0017 g (9.05×10^{-6} mol) *p*-toluenesulfonic acid, and 25 ml of toluene. The flask was fitted with a Hickman still and condenser and the solution was refluxed for 16 h. After this time, the toluene was removed under reduced pressure and the resulting brown solid was purified by column chromatography (SiO_2, 95% hexane/5% EtOAc) to produce 0.395 g (79%) of product. Yellow needles for the diffraction study were crystallized from methylene chloride solution (m.p. 420 K). ATR–IR (cm^{-1}) 3063, 2962, 1640, 838, 816, 732; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (*dd*, 1H), 7.63 (*dd*, 2H), 7.44 (*dt*, 1H), 7.40 (*m*, 4H), 7.00 (*m*, 3H), 6.68 (*d*, 1H); ^{13}C (75 MHz, $CDCl_3$): δ 163.45, 150.22, 143.97, 141.90, 137.32, 132.11, 132.08, 131.06, 129.46, 129.32, 128.54, 127.78, 127.03, 123.39, 120.40, 119.83, 119.70. FTIR, ^{1}H NMR, COSY and ^{13}C NMR are given in the supplementary materials.

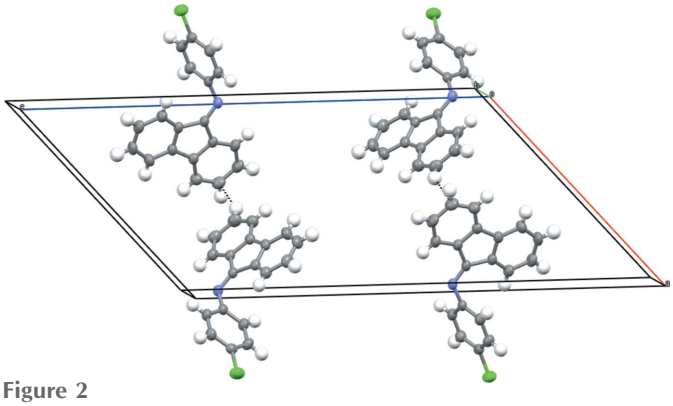


Figure 2
The unit-cell packing in the title compound as viewed along [010]. The C—H···π contact is shown as a black dashed line.

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

*Cg*4 is the centroid of the C14–C19 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···*Cg*4	0.93	2.98	3.7347 (16)	139

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{12}ClN$
M_r	289.75
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	14.2842 (14), 5.2148 (2), 25.923 (3)
β (°)	132.024 (17)
V (Å^3)	1434.5 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.45 × 0.21 × 0.20
Data collection	
Diffractometer	Rigaku Oxford Diffraction Xcalibur, Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.767, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35328, 5301, 3925
R_{int}	0.031
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.780
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.050, 0.134, 1.03
No. of reflections	5301
No. of parameters	190
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.36

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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full crystallographic data

IUCrData (2019). **4**, x190555 [https://doi.org/10.1107/S2414314619005558]

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Crystal data

$C_{19}H_{12}ClN$
M_r = 289.75
Monoclinic, $P2_1/c$
a = 14.2842 (14) Å
b = 5.2148 (2) Å
c = 25.923 (3) Å
β = 132.024 (17)°
V = 1434.5 (2) Å^3
Z = 4
$F(000)$ = 600
D_x = 1.342 Mg m^{-3}
Melting point: 420 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7600 reflections
θ = 4.5–32.3°
μ = 0.26 mm^{-1}
T = 293 K
Needle, yellow
0.45 × 0.21 × 0.20 mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015)
T_{min} = 0.767, T_{max} = 1.000
35328 measured reflections
5301 independent reflections
3925 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 33.7°, θ_{min} = 4.2°
h = −21→21
k = −8→7
l = −38→39

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.134
S = 1.03
5301 reflections
190 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.4392P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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. The H atoms were included in calculated positions (C—H = 0.93Å) and refined as riding with Uĩso~ = 1.2U_{eq} (carrier atom).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	−0.45087 (4)	0.83251 (10)	0.46185 (2)	0.06331 (14)
N1	0.00458 (10)	0.2458 (2)	0.57276 (5)	0.0404 (2)
C1	0.09621 (12)	0.2050 (2)	0.63725 (6)	0.0355 (2)
C2	0.12964 (12)	0.3141 (2)	0.70134 (6)	0.0362 (2)
C3	0.07819 (14)	0.5127 (3)	0.71103 (7)	0.0443 (3)
H3	0.0092	0.6045	0.6734	0.053*
C4	0.13234 (15)	0.5717 (3)	0.77866 (8)	0.0521 (4)
H4	0.0984	0.7032	0.7860	0.063*
C5	0.23516 (16)	0.4380 (4)	0.83459 (8)	0.0545 (4)
H5	0.2686	0.4785	0.8791	0.065*
C6	0.28949 (15)	0.2448 (3)	0.82579 (7)	0.0495 (3)
H6	0.3596	0.1566	0.8638	0.059*
C7	0.23708 (12)	0.1852 (3)	0.75893 (7)	0.0383 (3)
C8	0.27774 (12)	−0.0020 (3)	0.73491 (6)	0.0375 (3)
C9	0.37545 (14)	−0.1769 (3)	0.77105 (8)	0.0481 (3)
H9	0.4302	−0.1882	0.8192	0.058*
C10	0.38990 (16)	−0.3354 (3)	0.73379 (9)	0.0537 (4)
H10	0.4555	−0.4535	0.7573	0.064*
C11	0.30817 (15)	−0.3205 (3)	0.66212 (9)	0.0516 (4)
H11	0.3199	−0.4283	0.6383	0.062*
C12	0.20892 (13)	−0.1468 (3)	0.62532 (7)	0.0441 (3)
H12	0.1532	−0.1386	0.5771	0.053*
C13	0.19547 (12)	0.0136 (2)	0.66253 (6)	0.0360 (2)
C14	−0.10002 (12)	0.3955 (3)	0.54933 (6)	0.0373 (3)
C15	−0.13495 (13)	0.6099 (3)	0.50817 (7)	0.0425 (3)
H15	−0.0860	0.6625	0.4984	0.051*
C16	−0.24244 (14)	0.7457 (3)	0.48156 (7)	0.0460 (3)
H16	−0.2651	0.8912	0.4547	0.055*
C17	−0.31558 (12)	0.6632 (3)	0.49532 (7)	0.0426 (3)
C18	−0.28392 (14)	0.4484 (3)	0.53493 (8)	0.0477 (3)
H18	−0.3345	0.3942	0.5435	0.057*
C19	−0.17632 (14)	0.3145 (3)	0.56179 (8)	0.0456 (3)
H19	−0.1545	0.1687	0.5885	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0434 (2)	0.0768 (3)	0.0626 (2)	−0.01057 (18)	0.03256 (19)	0.0050 (2)
N1	0.0410 (5)	0.0500 (6)	0.0365 (5)	−0.0016 (5)	0.0285 (5)	0.0018 (5)

C1	0.0387 (6)	0.0387 (6)	0.0366 (6)	0.0032 (5)	0.0283 (5)	0.0029 (5)
C2	0.0398 (6)	0.0382 (6)	0.0381 (6)	0.0052 (5)	0.0292 (5)	0.0057 (5)
C3	0.0463 (7)	0.0457 (7)	0.0460 (7)	0.0008 (6)	0.0330 (6)	0.0067 (6)
C4	0.0576 (8)	0.0556 (9)	0.0557 (8)	0.0057 (7)	0.0431 (8)	0.0174 (7)
C5	0.0591 (9)	0.0689 (10)	0.0416 (7)	0.0081 (8)	0.0363 (7)	0.0162 (7)
C6	0.0509 (8)	0.0590 (9)	0.0361 (6)	0.0022 (7)	0.0281 (6)	0.0047 (6)
C7	0.0421 (6)	0.0410 (6)	0.0373 (6)	0.0056 (5)	0.0288 (5)	0.0044 (5)
C8	0.0405 (6)	0.0379 (6)	0.0393 (6)	0.0034 (5)	0.0289 (5)	0.0021 (5)
C9	0.0472 (7)	0.0489 (8)	0.0463 (7)	−0.0053 (6)	0.0304 (6)	−0.0048 (6)
C10	0.0517 (8)	0.0469 (8)	0.0658 (10)	−0.0086 (6)	0.0407 (8)	−0.0033 (7)
C11	0.0542 (8)	0.0486 (8)	0.0640 (9)	−0.0005 (6)	0.0444 (8)	0.0097 (7)
C12	0.0468 (7)	0.0488 (7)	0.0462 (7)	0.0036 (6)	0.0351 (6)	0.0082 (6)
C13	0.0388 (6)	0.0376 (6)	0.0393 (6)	0.0033 (5)	0.0292 (5)	0.0035 (5)
C14	0.0372 (6)	0.0465 (7)	0.0319 (5)	0.0017 (5)	0.0246 (5)	0.0048 (5)
C15	0.0449 (7)	0.0513 (8)	0.0413 (6)	0.0007 (6)	0.0330 (6)	−0.0006 (6)
C16	0.0486 (7)	0.0505 (8)	0.0416 (7)	−0.0043 (6)	0.0314 (6)	−0.0045 (6)
C17	0.0357 (6)	0.0525 (8)	0.0372 (6)	0.0007 (5)	0.0234 (5)	0.0096 (6)
C18	0.0453 (7)	0.0559 (8)	0.0544 (8)	0.0052 (6)	0.0385 (7)	0.0043 (7)
C19	0.0482 (7)	0.0502 (8)	0.0488 (7)	0.0000 (6)	0.0367 (6)	−0.0034 (6)

Geometric parameters (Å, º)

Cl1—C17	1.7384 (14)	C9—H9	0.9300
N1—C1	1.2742 (17)	C9—C10	1.388 (2)
N1—C14	1.4127 (17)	C10—H10	0.9300
C1—C2	1.4999 (16)	C10—C11	1.384 (2)
C1—C13	1.4805 (18)	C11—H11	0.9300
C2—C3	1.3869 (18)	C11—C12	1.389 (2)
C2—C7	1.4029 (19)	C12—H12	0.9300
C3—H3	0.9300	C12—C13	1.3840 (17)
C3—C4	1.397 (2)	C14—C15	1.3870 (19)
C4—H4	0.9300	C14—C19	1.3936 (18)
C4—C5	1.376 (2)	C15—H15	0.9300
C5—H5	0.9300	C15—C16	1.384 (2)
C5—C6	1.381 (2)	C16—H16	0.9300
C6—H6	0.9300	C16—C17	1.379 (2)
C6—C7	1.3871 (18)	C17—C18	1.375 (2)
C7—C8	1.4702 (18)	C18—H18	0.9300
C8—C9	1.381 (2)	C18—C19	1.379 (2)
C8—C13	1.3986 (18)	C19—H19	0.9300
C1—N1—C14	121.21 (10)	C11—C10—C9	121.05 (14)
N1—C1—C2	132.51 (12)	C11—C10—H10	119.5
N1—C1—C13	122.11 (11)	C10—C11—H11	119.5
C13—C1—C2	105.36 (10)	C10—C11—C12	120.96 (13)
C3—C2—C1	132.03 (13)	C12—C11—H11	119.5
C3—C2—C7	120.00 (12)	C11—C12—H12	121.0
C7—C2—C1	107.90 (11)	C13—C12—C11	118.00 (13)

C2—C3—H3	120.8	C13—C12—H12	121.0
C2—C3—C4	118.46 (14)	C8—C13—C1	109.18 (10)
C4—C3—H3	120.8	C12—C13—C1	129.62 (12)
C3—C4—H4	119.5	C12—C13—C8	121.06 (12)
C5—C4—C3	120.97 (14)	C15—C14—N1	120.55 (11)
C5—C4—H4	119.5	C15—C14—C19	119.23 (12)
C4—C5—H5	119.4	C19—C14—N1	119.92 (12)
C4—C5—C6	121.13 (13)	C14—C15—H15	119.9
C6—C5—H5	119.4	C16—C15—C14	120.22 (12)
C5—C6—H6	120.8	C16—C15—H15	119.9
C5—C6—C7	118.49 (14)	C15—C16—H16	120.3
C7—C6—H6	120.8	C17—C16—C15	119.39 (14)
C2—C7—C8	109.16 (11)	C17—C16—H16	120.3
C6—C7—C2	120.88 (13)	C16—C17—Cl1	119.58 (12)
C6—C7—C8	129.95 (13)	C18—C17—Cl1	119.11 (11)
C9—C8—C7	131.12 (12)	C18—C17—C16	121.31 (13)
C9—C8—C13	120.55 (12)	C17—C18—H18	120.4
C13—C8—C7	108.32 (11)	C17—C18—C19	119.19 (13)
C8—C9—H9	120.8	C19—C18—H18	120.4
C8—C9—C10	118.37 (14)	C14—C19—H19	119.7
C10—C9—H9	120.8	C18—C19—C14	120.62 (14)
C9—C10—H10	119.5	C18—C19—H19	119.7

Hydrogen-bond geometry (Å, º)

*Cg*4 is the centroid of the C14–C19 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···*Cg*4	0.93	2.98	3.7347 (16)	139