

***N*-(9*H*-Fluoren-9-ylidene)-*N*-(4-methoxyphenyl)-amine**

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**Key indicators**

Single-crystal X-ray study

*T* = 100 K

Mean  $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

*R* factor = 0.042

*wR* factor = 0.115

Data-to-parameter ratio = 17.9

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

The title compound,  $\text{C}_{20}\text{H}_{15}\text{NO}$ , was synthesized by the *p*-toluenesulfonic acid-assisted Schiff base reaction between 9-fluorenone and 4-methoxyaniline. The crystal structure of the title compound has been determined at 100 K.

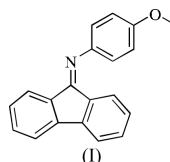
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**Comment**

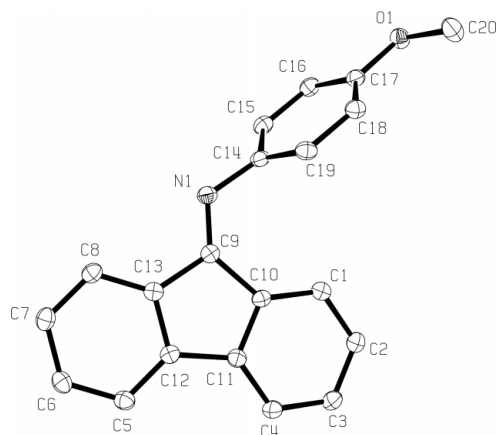
The chemistry of imines has enjoyed renewed interest in the synthetic organic and organometallic disciplines. The use of imines in the formation of aromatic heterocycles (Weinreb & Scola, 1989; Kel'in *et al.*, 2001; Doyle *et al.*, 2003) and  $\beta$ -lactams (Hart & Ha, 1989) has seen the utility of the imine functionality increase dramatically in organic synthesis. Imines have also been used successfully as starting materials in the formation of chiral amines (Porter *et al.*, 2001) and in enantioselective Diels–Alder reactions (Kobayashi & Ishitari, 1999). In addition, imines have found utility as ligands in the formation of chiral transition metal complexes (Davis & Arndtsen, 2000; Baar *et al.*, 2000). These and other advances in imine chemistry have prompted our group to investigate the formation of imines for use in the resolution of racemic mixtures of aldehydes and ketones. Chiral amines can form Schiff bases with racemic aldehydes and ketones to form diastereomeric mixtures of imines. These diastereomers can be resolved either through flash chromatography or differential recrystallization.



The title compound, (I) (Fig. 1), is not chiral, however, and was synthesized in order to determine the viability of imine formation conditions. Large orange crystals of (I) were obtained after column chromatography using an 80/20 (by volume) mixture of hexanes and ethyl acetate. Compound (I) crystallizes in a general position. The benzene ring bound to the imine N atom bears a methoxy group that is nearly coplanar. To avoid unfavorable steric interactions between H atoms on atoms C1 and C19, the substituent benzene ring has a dihedral angle of  $68.08(11)^\circ$  with respect to the 9*H*-fluoren-9-imine unit. The C9–N1–C14 angle of  $122.16(9)^\circ$  and the N1–C9 bond distance of  $1.2808(12) \text{ \AA}$  are in close agreement with the two published structures of the similar *N*-fluorenylideneaniline (Peters *et al.*, 1998; Pierre *et al.*, 1997).

**Experimental**

To a 100 ml round-bottomed flask equipped with a Hickman still and reflux condenser was added 9-fluorenone (2.5 g, 14 mmol), 4-meth-


**Figure 1**

A view of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

oxyaniline (2.06 g, 16.8 mmol), *p*-toluenesulfonic acid (0.014 g, 74  $\mu$ mol) and toluene (50 ml). The resulting mixture was heated under reflux for 24 h. After this time, the resulting black solution was concentrated under reduced pressure, producing a black solid. The solid was purified by flash chromatography (SiO<sub>2</sub>, 80% hexanes-ethyl acetate), producing fluoren-9-ylidene-(4-methoxy-phenyl)-amine (3.36 g) as an orange solid (yield 84%). *R*<sub>f</sub> 0.64 (SiO<sub>2</sub>, 80% hexanes-ethyl acetate); m.p. 404.5–406.1 K; UV-vis (CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{\text{max}}$ , log  $\epsilon$ ): 420, 3.386; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 3049, 3004, 1644, 1236, 1033, 846, 791, 731, 654; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.924 (*d*, 1H, *J* = 7.4 Hz), 7.599 (*d*, 2H, *J* = 7.5 Hz), 7.462 (*t*, 1H, *J* = 7.4 Hz), 7.338 (*q*, 2H, *J* = 7.7 Hz), 6.970 (*m*, 5H), 6.736 (*d*, 1H, *J* = 7.7 Hz), 3.874 (*s*, 3H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  163.29, 156.62, 144.89, 143.74, 141.74, 137.62, 131.67, 131.62, 131.13, 128.34, 127.62, 126.86, 123.14, 120.14, 119.65, 119.52, 114.53, 55.47; MS calculated for C<sub>20</sub>H<sub>15</sub>NO: *M*<sup>+</sup> 285; measured: 285. Analysis calculated for C<sub>20</sub>H<sub>15</sub>NO: C 84.19, H 5.30, N 4.91%; found: C 83.95, H 5.53, N 4.89%.

#### Crystal data

C <sub>20</sub> H <sub>15</sub> NO	<i>D</i> <sub>x</sub> = 1.319 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 285.33	Mo <i>K</i> $\alpha$ radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 14 878 reflections
<i>a</i> = 19.0275 (10) Å	$\theta$ = 2.4–28.3°
<i>b</i> = 9.8262 (5) Å	$\mu$ = 0.08 mm <sup>-1</sup>
<i>c</i> = 17.4862 (10) Å	<i>T</i> = 100 (2) K
$\beta$ = 118.4860 (10)°	Parallelepiped, orange
<i>V</i> = 2873.5 (3) Å <sup>3</sup>	0.60 × 0.56 × 0.35 mm
<i>Z</i> = 8	

#### Data collection

Bruker SMART APEX CCD diffractometer	3565 independent reflections
$\omega$ scans	3287 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: multi-scan (SADABS in SAINT-Plus; Bruker, 1997–1999)	<i>R</i> <sub>int</sub> = 0.042
<i>T</i> <sub>min</sub> = 0.922, <i>T</i> <sub>max</sub> = 0.968	$\theta_{\text{max}}$ = 28.3°
14 415 measured reflections	<i>h</i> = –25 → 25
	<i>k</i> = –13 → 13
	<i>l</i> = –23 → 23

#### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0646P)^2 + 1.5364P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.115$	$(\Delta/\sigma)_{\text{max}} = 0.003$
<i>S</i> = 1.08	$\Delta\rho_{\text{max}} = 0.37 \text{ e } \text{Å}^{-3}$
3287 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{Å}^{-3}$
199 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

O1–C17	1.3761 (11)	C16–C17	1.3971 (14)
O1–C20	1.4231 (13)	C7–C8	1.3947 (14)
N1–C9	1.2808 (12)	C7–C6	1.3950 (14)
N1–C14	1.4189 (13)	C12–C5	1.3879 (13)
C19–C14	1.3914 (14)	C12–C13	1.4021 (13)
C19–C18	1.3954 (14)	C12–C11	1.4713 (13)
C9–C13	1.4876 (13)	C13–C8	1.3844 (13)
C9–C10	1.4989 (13)	C5–C6	1.3954 (14)
C18–C17	1.3914 (13)	C4–C11	1.3859 (13)
C10–C1	1.3898 (14)	C4–C3	1.3924 (14)
C10–C11	1.4124 (13)	C1–C2	1.3986 (14)
C15–C16	1.3845 (14)	C3–C2	1.3915 (14)
C15–C14	1.4003 (13)		
C17–O1–C20	116.78 (8)	C13–C12–C11	108.28 (8)
C9–N1–C14	122.16 (9)	C8–C13–C12	121.29 (9)
C14–C19–C18	121.00 (9)	C8–C13–C9	129.56 (9)
N1–C9–C13	121.07 (9)	C12–C13–C9	109.12 (8)
N1–C9–C10	133.31 (9)	C12–C5–C6	118.08 (9)
C13–C9–C10	105.57 (8)	O1–C17–C18	124.19 (9)
C17–C18–C19	119.44 (9)	O1–C17–C16	115.74 (8)
C1–C10–C11	119.80 (9)	C18–C17–C16	120.08 (9)
C1–C10–C9	132.31 (9)	C11–C4–C3	118.38 (9)
C11–C10–C9	107.68 (8)	C10–C1–C2	118.59 (9)
C16–C15–C14	120.63 (9)	C4–C11–C10	121.38 (9)
C19–C14–C15	118.85 (9)	C4–C11–C12	129.15 (9)
C19–C14–N1	121.76 (9)	C10–C11–C12	109.32 (8)
C15–C14–N1	118.95 (9)	C13–C8–C7	118.29 (9)
C15–C16–C17	119.97 (9)	C2–C3–C4	120.67 (9)
C8–C7–C6	120.45 (9)	C3–C2–C1	121.15 (10)
C5–C12–C13	120.57 (9)	C7–C6–C5	121.31 (9)
C5–C12–C11	131.05 (9)		

All H atoms were included in calculated positions, with aromatic and methyl C–H distances of 0.95 and 0.98 Å, respectively, and were included in the refinement as riding, with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub> of the carrier atom.

Data collection: *SMART* (Bruker, 1997–1999); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1997–1999); 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: *SHELXTL-Plus* (Sheldrick, 1990).

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