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***N*-(9*H*-Fluoren-9-ylidene)-*N*-(2-methoxyphenyl)amine**

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Key indicators

Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.051
 wR factor = 0.139
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>.

N-(9*H*-Fluoren-9-ylidene)-*N*-(2-methoxyphenyl)amine

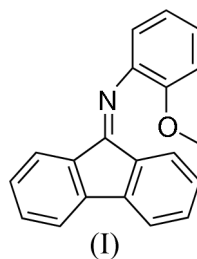
The title compound, alternatively called *N*-(9*H*-fluoren-9-ylidene)-2-methoxyaniline, $\text{C}_{20}\text{H}_{15}\text{NO}$, was synthesized by the *p*-toluenesulfonic acid-assisted Schiff base reaction between 9-fluorenone and 2-methoxyaniline. The crystal structure of the title compound has been determined at 100 K.

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Comment

The imine functionality has many practical applications in organic synthesis. Imines have been used to produce chiral nitrogen-containing natural products *via* reaction with allylic titanium compounds (Gao & Sato, 1995), *via* enantioselective reductive amination (Chi *et al.*, 2003), *via* the nucleophilic addition of dialkylzinc reagents (Boezio *et al.*, 2003), and *via* camphor-derived mercapto chiral auxiliaries (Yang *et al.*, 1994). Our interest in imines involves their use as resolving agents for racemic aldehydes and ketones. Chiral amines will form diastereomeric imines that can be separated to yield enantiomerically pure carbonyl compounds.

The title compound, (I) (Fig. 1), is not chiral, however, and was synthesized to determine what effects *ortho* substituents will have on imine formation. In comparison with a closely related imine, namely *N*-(9*H*-fluoren-9-ylidene)-4-methoxyaniline (Glagovich *et al.*, 2004*a*), where the methoxy group is *para* to the imine N atom, the title compound formed in slightly lower yield, but not appreciably so. Large orange crystals of (I) were obtained after column chromatography using a 90:10 (by volume) mixture of hexanes and ethyl acetate.



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 C1 and C19, the substituent benzene ring makes a dihedral angle of $84.00(2)^\circ$ with the 9*H*-fluorene-9-imine unit. The $\text{C}9-\text{N}1-\text{C}14$ angle of $120.75(11)^\circ$ and the $\text{N}1-\text{C}9$ bond distance of $1.2746(16)$ Å are in close agreement with the published structures of the two compounds *N*-(9*H*-fluoren-9-ylidene)-*N*-(4-methoxyphenyl)amine (Glagovich *et al.*, 2004*a*) and *N*-9*H*-fluoren-9-ylidene-3,4-dimethylaniline (Glagovich *et al.*, 2004*b*).

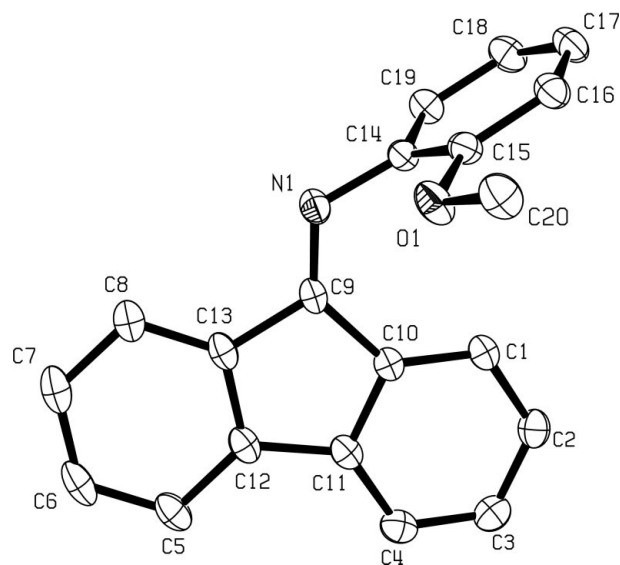


Figure 1
A view of (I) (ORTEP-3; Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted.

Experimental

In a 50 ml round-bottomed flask equipped with a Hickman still and a reflux condenser were combined 9-fluorenone (0.367 g, 2.04 mmol), *o*-anisidine (0.502 g, 4.08 mmol), *p*-toluenesulfonic acid (0.0021 g, 10 μ mol) and toluene (20 ml). The resulting mixture was refluxed for 20 h. After this time, the resulting black solution was concentrated under reduced pressure to produce a black oil. The oil was purified by flash chromatography (Al_2O_3 , 90% hexanes–ethyl acetate), which yielded 0.462 g of (I) as an orange solid (79.4%). Analysis: R_F 0.46 (Al_2O_3 , 90% hexanes–ethyl acetate); m.p. 407.8 K; IR (CHCl_3 , ν , cm^{-1}): 3057, 2991, 1656, 1248, 1017, 744; ^1H NMR (300 MHz, CDCl_3 , δ , p.p.m.): 8.014 (*d*, 1H, $J = 7.4$ Hz), 7.593 (*d*, 2H, $J = 7.4$ Hz), 7.462 (*t*, 1H, $J = 7.5$ Hz), 7.351 (*t*, 1H, $J = 7.5$ Hz), 7.325 (*t*, 1H, $J = 7.5$ Hz), 7.191 (*t*, 1H, $J = 7.5$ Hz), 7.191 (*t*, 1H, $J = 7.5$ Hz), 7.102 (*d*, 1H, $J = 7.4$ Hz), 6.947 (*t*, 1H, $J = 7.5$ Hz), 6.936 (*d*, 1H, $J = 7.4$ Hz), 6.688 (*d*, 1H, $J = 7.4$ Hz); ^{13}C NMR (300 MHz, CDCl_3 , δ , p.p.m.): 159.17, 148.79, 143.59, 141.89, 140.89, 137.55, 131.90, 131.78, 131.74, 128.41, 127.86, 1226.46, 125.04, 123.57, 121.22, 120.08, 119.56, 119.53, 111.76, 55.78; UV–Vis (CH_2Cl_2 ; λ_{max} , log ϵ , nm): 406, 1707; MS: calculated for $\text{C}_{20}\text{H}_{15}\text{NO}$: M^+ : 285, measured: 285.

Crystal data

$\text{C}_{20}\text{H}_{15}\text{NO}$
 $M_r = 285.33$
Monoclinic, $P2_1/c$
 $a = 11.0517$ (5) \AA
 $b = 9.3304$ (4) \AA
 $c = 15.6876$ (9) \AA
 $\beta = 116.832$ (1) $^\circ$
 $V = 1443.49$ (12) \AA^3
 $Z = 4$

$D_x = 1.313$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 300 reflections
 $\theta = 2.2$ – 31.7 $^\circ$
 $\mu = 0.08$ mm^{-1}
 $T = 100$ (2) K
Block, orange
 $0.6 \times 0.6 \times 0.5$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.951$, $T_{\text{max}} = 0.960$
12 925 measured reflections

3578 independent reflections
3381 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 28.3$ $^\circ$
 $h = -14 \rightarrow 14$
 $k = -12 \rightarrow 12$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.139$
 $S = 1.09$
3578 reflections
200 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.4989P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.45$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.23$ e \AA^{-3}

H atoms were included in calculated positions, with a C–H distance of 0.95 \AA , and were included in the riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom.

Data collection: SMART (Bruker, 1997–1999); cell refinement: SAINT-Plus (Bruker, 1997–1999); data reduction: SAINT-Plus; 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: SHELXL97.

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