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N,N'-Bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine

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Key indicators

Single-crystal X-ray study
 T = 100 K
 Mean $\sigma(\text{C}-\text{C}) = 0.016 \text{ \AA}$
 R factor = 0.047
 wR factor = 0.117
 Data-to-parameter ratio = 17.4

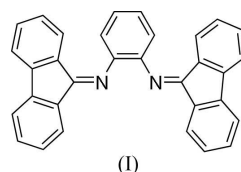
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_{32}\text{H}_{20}\text{N}_2$, was synthesized by the *p*-toluenesulfonic acid-assisted Schiff base reaction between 9-fluorenone and *o*-phenylenediamine. The molecule crystallizes in a centrosymmetric space group and is located on a twofold rotation axis. The two fluoren-9-ylidene moieties adopt a *trans* configuration as substituents on the linking benzene ring, making the entire molecule chiral.

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Comment

Diimines have been used as ligands in transition metal catalysis for a number of years (Fache *et al.*, 2000; Müller & Fruit, 2003; Walsh *et al.*, 2003). Most of the diimines used, however, are achiral (Costa *et al.*, 2002; Desvergnès-Breuil *et al.*, 2003; Wilker *et al.*, 1991) with a few exceptions (Mimoun *et al.*, 1999; Chavarot *et al.*, 2003). These exceptional chiral diimines have all been derivatives of *trans*-1,2-diaminocyclohexane. We present the solid state structure of a chiral diimine, (I), consisting of aromatic subunits.



N,N'-Bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (Fig. 1 and Table 1), is a chiral aromatic diimine crystallizing as a racemic mixture in the centrosymmetric space group $C2/c$. The molecule, which sits on a site of twofold rotation symmetry,

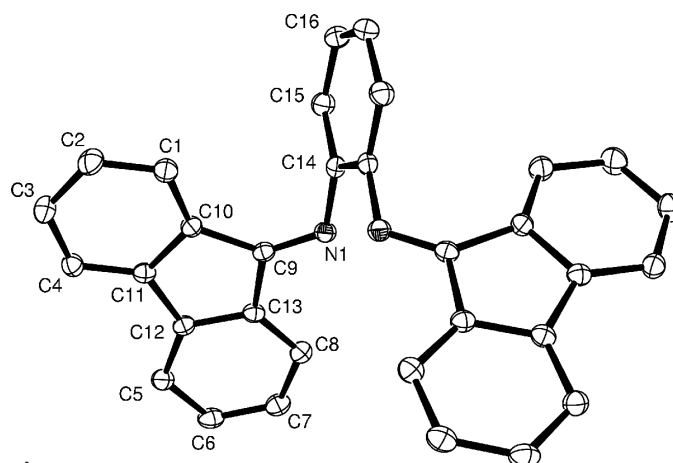


Figure 1

A view of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity and the numbering scheme is given for the asymmetric unit.

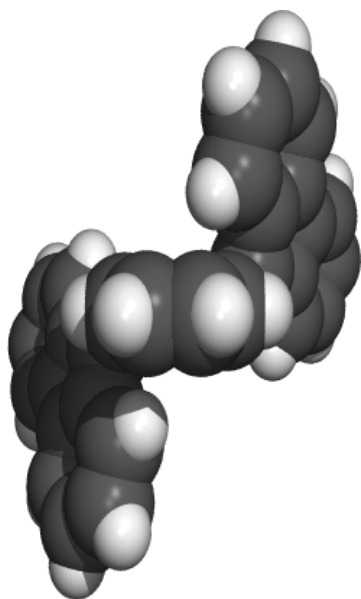


Figure 2
Space filling view of (I), down the twofold symmetry axis (Persistence of Vision Pty, 2004).

owes its chirality to the *trans* orientation of the two fluoren-9-ylidene moieties with respect to the central benzene ring (Fig. 2). The angle between the mean plane of the fluoren-9-ylidene portion and the bridging benzene ring is 76.89 (8)° and the *trans* orientation makes bidentate metal binding from this ligand improbable. The steric bulk of the two fluoren-9-ylidene units around the central benzene ring precludes the two groups from adopting a *syn* geometry. A variety of aromatic imines have been synthesized in this laboratory (Glagovich *et al.*, 2004*a,b,c*), but the title compound represents the first diimine synthesized. Several more diimines related to the title compound (*via* the reactions of 9-fluorenone with both *m*- and *p*-phenylenediamine) are currently being synthesized. These compounds will probably be achiral, as the two fluoren-9-ylidene moieties are further apart and thus less likely to interfere with each other sterically.

Experimental

To a 100 ml round-bottomed flask equipped with a Hickman still and a reflux condenser were added *o*-phenylenediamine (0.5 g, 4.6 mmol), 9-fluorenone (1.5 g, 8.3 mmol), *p*-toluenesulfonic acid (0.0004 g, 2.3 μmol) and toluene (40 ml). The resulting mixture was heated with refluxing for 24 h. After this time, the orange solution was concentrated under reduced pressure, producing a red solid. The solid was purified by flash chromatography (SiO₂, 90% hexanes–ethyl acetate), yielding 0.93 g of *N,N'*-bis(9*H*-fluoren-9-ylidene)benzene-1,2-diamine (overall yield of 46.5%) as a red solid containing many crystals with well defined morphologies. Analysis: *R*_f 0.32 (SiO₂, 90% hexanes–ethyl acetate); m.p. 485; IR (CHCl₃): 3077, 3056, 3039, 1651, 1642, 1463, 1450, 1377, 1307, 1102, 944, 791, 727 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.690 (*d*, 2H, *J* = 7.5 Hz), 7.525 (*d*, 2H, *J* = 7.5 Hz), 7.485 (*d*, 2H, *J* = 7.5 Hz), 7.342 (*t*, 2H, *J* = 7.5 Hz), 7.300 (*t*, 2H, *J* = 7.5 Hz), 7.235 (*dd*, 2H, *J* = 7.0 and 3.6 Hz), 7.186 (*t*, 2H, *J* = 9.2 Hz), 7.176 (*t*, 2H, *J* = 9.2 Hz), 7.090 (*dd*, 2H, *J* = 7.0 and 3.6 Hz), 6.991 (*t*,

2H, *J* = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 163.92, 163.02, 143.82, 141.92, 141.08, 137.88, 131.92, 131.74, 128.45, 127.91, 127.19, 125.14, 123.68, 120.25, 119.93, 119.56; UV/vis (CH₂Cl₂, λ_{max}, log ε): 406, 4685 nm; MS, calculated for C₃₂H₂₀N₂: *M*⁺: 432, measured: 432.

Crystal data

C₃₂H₂₀N₂
*M*_r = 432.50
 Monoclinic, *C*2/*c*
a = 14.9807 (6) Å
b = 15.5273 (6) Å
c = 9.4228 (4) Å
 β = 99.962 (1)°
V = 2158.79 (15) Å³
Z = 4

*D*_x = 1.331 Mg m⁻³
 Mo Kα radiation
 Cell parameters from 9442 reflections
 θ = 2.6–32.1°
 μ = 0.08 mm⁻¹
T = 100 (2) K
 Irregular fragment, red
 0.48 × 0.20 × 0.14 mm

Data collection

Bruker SMART APEX diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
*T*_{min} = 0.903, *T*_{max} = 0.986
 11 410 measured reflections

2685 independent reflections
 2573 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.023
 θ_{max} = 28.3°
h = -19 → 19
k = -20 → 20
l = -12 → 12

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.047
wR (*F*²) = 0.117
S = 1.07
 2685 reflections
 154 parameters
 H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0569*P*)² + 2.0007*P*]
 where *P* = (*F*_o² + 2*F*_c²)/3
 (Δ/σ)_{max} < 0.001
 Δρ_{max} = 0.40 e Å⁻³
 Δρ_{min} = -0.25 e Å⁻³
 Extinction correction: none

Table 1

Selected geometric parameters (Å, °).

N1—C9	1.2818 (15)	C9—C10	1.4980 (15)
N1—C14	1.4133 (14)	C14—C14 ⁱ	1.405 (2)
C9—C13	1.4868 (15)		
C9—N1—C14	120.48 (10)	C15—C14—C14 ⁱ	118.90 (7)
N1—C9—C13	121.49 (10)	C15—C14—N1	120.08 (10)
N1—C9—C10	132.69 (10)	C14 ⁱ —C14—N1	120.67 (6)
C13—C9—C10	105.68 (9)		

Symmetry code: (i) -*x*, *y*, -*z* + ½.

H atoms were included in calculated positions, with a C—H distance of 0.95 Å, and were refined in the riding-model approximation, with *U*_{iso}(H) = 1.2*U*_{eq}(C) of the carrier atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE-Plus* (Bruker, 1999); data reduction: *SAINTE-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997) and *POV-Ray* (Persistence of Vision Pty, 2004); software used to prepare material for publication: *SHELXL97*.

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References

- Bruker (1999). *SMART* and *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chavarot, M., Ménage, S., Hamelin, O., Charnay, F., Pécaut, J. & Fontecave, M. (2003). *Inorg. Chem.* **42**, 4810–4816.
- Costa, A. M., Jimeno, C., Gavenonis, J., Carroll, P. J. & Walsh, P. J. (2002). *J. Am. Chem. Soc.* **124**, 6929–6941.
- Desvergnès-Breuil, V., Hebbe, V., Dietrich-Buchecker, C., Sauvage, J.-P. & Lacour, J. (2003). *Inorg. Chem.* **42**, 255–257.
- Fache, F., Schulz, E., Tommasino, M. L. & Lemaire, M. (2000). *Chem. Rev.* **100**, 2159–2231.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Glagovich, N., Reed, E., Crundwell, G., Updergraff, J. B. III, Zeller, M. & Hunter, A. D. (2004a). *Acta Cryst.* **E60**, o623–o625.
- Glagovich, N. M., Reed, E. M., Crundwell, G., Updergraff, J. B. III, Zeller, M. & Hunter, A. D. (2004b). *Acta Cryst.* **E60**, o1269–o1270.
- Glagovich, N. M., Reed, E. M., Crundwell, G., Updergraff, J. B. III, Zeller, M. & Hunter, A. D. (2004c). *Acta Cryst.* **E60**, o2000–o2001.
- Mimoun, H., de Saint Laumer, J. Y., Giannini, L., Scopelliti, R. & Floriani, C. (1999). *J. Am. Chem. Soc.* **121**, 6158–6166.
- Müller, P. & Fruit, C. (2003). *Chem. Rev.* **103**, 2905–2919.
- Persistence of Vision Pty (2004). Persistence of Vision Raytracer (POV-Ray). Version 3.6. <http://www.povray.org/download/>.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Walsh, P. J., Lurain, A. E. & Balsells, J. (2003). *Chem. Rev.* **103**, 3297–3344.
- Wilker, J. J., Gelasco, A., Pressler, M. A., Day, R. O. & Maroney, M. J. (1991). *J. Am. Chem. Soc.* **113**, 6342–6343.