

9,9-Bis(4-methoxyphenyl)-9H-cyclopenta[2,1-*b*:3,4-*b'*]dipyridine

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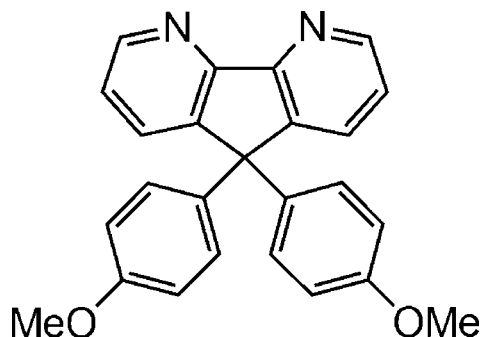
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.091; wR factor = 0.147; data-to-parameter ratio = 9.8.

The title compound, $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2$, was synthesized by the Friedel–Crafts reaction of 4,5-diazafluorene-9-one with anisole in the presence of H_2SO_4 . The molecule is located on a twofold rotation axis. The 4,5-diazafluorene (cyclopenta[2,1-*b*:3,4-*b'*]dipyridine) ring system is planar. The molecular packing is characterized by a columnar structure along the c axis. The methoxyphenyl groups overlap each other in the column. The interplanar distance and the centroid–centroid distances between the benzene rings are 3.87 (1) and 4.07 (1) Å, respectively. The 4,5-diazafluorene units form a coil-like structure.

Related literature

The title compound was reported to be an electron-transporting and hole-blocking material in the study of electroluminescent (EL) devices (Ono *et al.*, 2004). For related literature on molecular structures including the 4,5-diazafluorene ring system, see: Ono *et al.* (2007); Riklin *et al.* (1999); Fun *et al.* (1995); Lu *et al.* (1995, 2000).



Experimental

Crystal data

$\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2$
 $M_r = 380.45$
 Tetragonal, $P4_12_12$
 $a = 11.607$ (3) Å
 $c = 14.101$ (4) Å
 $V = 1899.7$ (8) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.09$ mm⁻¹
 $T = 296$ (1) K
 $0.45 \times 0.15 \times 0.15$ mm

Data collection

Rigaku/MSM Mercury CCD diffractometer
 Absorption correction: none
 19259 measured reflections

1302 independent reflections
 1241 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.091$
 $wR(F^2) = 0.147$
 $S = 1.44$
 1302 reflections

133 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.16$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³

Data collection: *CrystalClear* (Rigaku/MSM, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2226).

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supplementary materials

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9,9-Bis(4-methoxyphenyl)-9*H*-cyclopenta[2,1-*b*:3,4-*b'*]dipyridine

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Comment

The title compound, (I), was prepared and investigated for electron-transporting layers in the study of organic electroluminescent (EL) devices (Ono *et al.*, 2004). Phosphorescent EL devices fabricated by (I) and Ir(ppy)₃ demonstrated high external quantum efficiencies due to the high hole-blocking ability of (I). One of the phosphorescent EL devices exhibited a maximum external quantum efficiency of 18%. This value is close to the theoretical limit about 20% from simple classical optics. With regard to the electron-transporting and hole-blocking abilities, the molecular arrangement of (I) has attracted considerable attention. In this paper, we report the crystal structure of (I).

The compound, (I), crystallizes in the *P*4₁2₁2 space group and is located on a twofold rotation axis. The molecular structure is shown in Fig. 1. The bond lengths and angles are all within the expected ranges. The 4,5-diazafluorene (cyclopenta[2,1-*b*:3,4-*b'*]dipyridine) ring system and the two methoxyphenyl groups are planar. The crystal structure is characterized by a columnar structure along the *c* axis, as shown in Fig. 2. The methoxyphenyl groups overlap each other in the column. The interplanar distance and the centroid-centroid distance between the benzene rings (C7—C12) at (*x*, *y*, *z*) and (−*y*, −*x*, −*z* + 3/2) are 3.87 (1) and 4.07 (1) Å, respectively. The diazafluorene moieties are arranged to form a coil-like structure.

Experimental

The title compound (I) was prepared as follows: Concentrated sulfuric acid (1.37 g, 14.0 mmol) was added dropwise to a mixture of 4,5-diazafluoren-9-one (0.50 g, 2.8 mmol) and anisole (1.19 g, 11.0 mmol). The mixture was stirred at 65 °C for 5 h. The red mixture was poured into water (50 ml). The aqueous solution was neutralized with aqueous NaOH and was extracted with dichloromethane (50 ml × 3). The organic solution was dried over Na₂SO₄ and concentrated. The residue was treated with active carbon and recrystallized from toluene to afford the compound of (I) (0.99 g, 95%) as colorless needles. Physical data for (I): m.p. 548–549 K; IR (KBr, cm^{−1}): 2949, 2830, 1562, 1507, 1402, 1250, 1179, 1040, 814, 747, 592, 513; ¹H NMR (CDCl₃, δ p.p.m.): 3.76 (s, 6H), 6.77 (d, *J* = 8.8 Hz, 4H), 7.08 (d, *J* = 8.8 Hz, 4H), 7.27 (dd, *J* = 7.8, 4.7 Hz, 2H), 7.74 (d, *J* = 7.8, 1.4 Hz, 2H), 8.72 (d, *J* = 4.7, 1.4 Hz, 2H); ¹³C NMR (CDCl₃, δ p.p.m.): 55.2, 60.2, 113.9, 123.4, 128.9, 133.5, 135.7, 146.2, 150.0, 157.4, 158.7; MS (EI): *m/z* 380 (*M*⁺), 365, 273. Anal. Calcd for C₂₅H₂₀N₂O₂: C, 78.93; H, 5.30; N, 7.36. Found: C, 78.72; H, 5.27; N, 7.16. Colorless crystals of (I) suitable for X-ray analysis were grown from a toluene solution.

Refinement

All the H atoms were placed in geometrically calculated positions [C—H = 0.93 (aromatic) or 0.96 (methyl) Å] and refined using a riding model, with *U*_{iso}(H) = 1.2*U*_{eq}(C) (aromatic) or 1.5*U*_{eq}(C) (methyl).

Figures

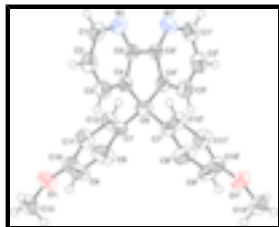


Fig. 1. The molecular structure of (I), with atom labels and 50% probability displacement ellipsoids for non-H atoms and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $y, x, -z + 1$].

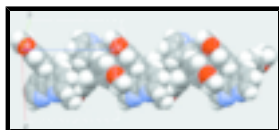


Fig. 2. The packing diagram of (I) stacked along the c axis.

9,9-Bis(4-methoxyphenyl)-9H-cyclopenta[2,1-*b*:3,4-*b'*]dipyridine

Crystal data

| | |
|-------------------------------|---|
| $C_{25}H_{20}N_2O_2$ | $Z = 4$ |
| $M_r = 380.45$ | $F_{000} = 800$ |
| Tetragonal, $P4_12_12$ | $D_x = 1.33 \text{ Mg m}^{-3}$ |
| Hall symbol: P 4abw 2nw | Melting point: 548 K |
| $a = 11.607(3) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 11.607(3) \text{ \AA}$ | $\lambda = 0.71073 \text{ \AA}$ |
| $c = 14.101(4) \text{ \AA}$ | Cell parameters from 4891 reflections |
| $\alpha = 90^\circ$ | $\theta = 3.4\text{--}27.5^\circ$ |
| $\beta = 90^\circ$ | $\mu = 0.09 \text{ mm}^{-1}$ |
| $\gamma = 90^\circ$ | $T = 296(1) \text{ K}$ |
| $V = 1899.7(8) \text{ \AA}^3$ | Block, colorless |
| | $0.45 \times 0.15 \times 0.15 \text{ mm}$ |

Data collection

| | |
|---|--|
| Rigaku/MSM Mercury CCD diffractometer | 1302 independent reflections |
| Radiation source: Rotating Anode | 1241 reflections with $I > 2\sigma(I)$ |
| Monochromator: Graphite Monochromator | $R_{\text{int}} = 0.075$ |
| Detector resolution: $14.6199 \text{ pixels mm}^{-1}$ | $\theta_{\text{max}} = 27.5^\circ$ |
| $T = 296(1) \text{ K}$ | $\theta_{\text{min}} = 3.4^\circ$ |
| φ & ω scans | $h = -13 \rightarrow 15$ |
| Absorption correction: none | $k = -12 \rightarrow 15$ |
| 19259 measured reflections | $l = -17 \rightarrow 18$ |

Refinement

| | |
|----------------------------|---|
| Refinement on F^2 | H-atom parameters constrained |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0183P)^2 + 1.2171P]$ |

$$R[F^2 > 2\sigma(F^2)] = 0.091$$

$$wR(F^2) = 0.147$$

$$S = 1.44$$

1302 reflections

133 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.15 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > 2\sigma(F^2)$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|------------|----------------------------------|
| C1 | 0.3328 (4) | 0.1272 (4) | 0.6615 (3) | 0.0523 (12) |
| C2 | 0.2771 (4) | 0.0298 (4) | 0.6906 (3) | 0.0546 (12) |
| C3 | 0.1809 (4) | -0.0082 (4) | 0.6424 (3) | 0.0508 (11) |
| C4 | 0.1441 (4) | 0.0559 (3) | 0.5655 (3) | 0.0385 (9) |
| C5 | 0.2069 (3) | 0.1531 (4) | 0.5412 (3) | 0.0385 (9) |
| C6 | 0.0393 (3) | 0.0393 (3) | 0.5000 | 0.0425 (13) |
| C7 | -0.0704 (3) | 0.0456 (4) | 0.5597 (3) | 0.0420 (10) |
| C8 | -0.1053 (5) | -0.0487 (4) | 0.6134 (4) | 0.0706 (16) |
| C9 | -0.1985 (4) | -0.0430 (4) | 0.6750 (4) | 0.0669 (15) |
| C10 | -0.2601 (4) | 0.0560 (4) | 0.6819 (3) | 0.0456 (10) |
| C11 | -0.2274 (4) | 0.1509 (4) | 0.6310 (3) | 0.0525 (12) |
| C12 | -0.1330 (4) | 0.1456 (4) | 0.5712 (3) | 0.0471 (10) |
| C13 | -0.3879 (4) | -0.0191 (5) | 0.7990 (3) | 0.0688 (15) |
| N1 | 0.3003 (3) | 0.1914 (3) | 0.5868 (2) | 0.0472 (9) |
| O1 | -0.3561 (3) | 0.0714 (3) | 0.7388 (2) | 0.0615 (9) |
| H1 | 0.3973 | 0.1507 | 0.6955 | 0.063* |
| H2 | 0.3041 | -0.0110 | 0.7428 | 0.066* |
| H3 | 0.1421 | -0.0746 | 0.6609 | 0.061* |
| H8 | -0.0650 | -0.1176 | 0.6079 | 0.085* |
| H9 | -0.2185 | -0.1067 | 0.7114 | 0.080* |
| H11 | -0.2688 | 0.2191 | 0.6366 | 0.063* |

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|------|---------|---------|--------|--------|
| H12 | -0.1111 | 0.2113 | 0.5380 | 0.056* |
| H13A | -0.4144 | -0.0831 | 0.7618 | 0.103* |
| H13B | -0.4486 | 0.0061 | 0.8404 | 0.103* |
| H13C | -0.3227 | -0.0424 | 0.8362 | 0.103* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C1 | 0.049 (3) | 0.062 (3) | 0.046 (2) | 0.006 (2) | -0.007 (2) | -0.008 (2) |
| C2 | 0.069 (3) | 0.054 (3) | 0.041 (2) | 0.015 (3) | -0.004 (2) | 0.001 (2) |
| C3 | 0.064 (3) | 0.040 (2) | 0.049 (2) | -0.002 (2) | 0.006 (2) | 0.001 (2) |
| C4 | 0.045 (2) | 0.033 (2) | 0.0371 (19) | 0.0025 (18) | 0.0056 (18) | -0.0065 (17) |
| C5 | 0.038 (2) | 0.039 (2) | 0.0389 (18) | 0.0002 (19) | 0.0024 (17) | -0.0075 (18) |
| C6 | 0.0374 (19) | 0.0374 (19) | 0.053 (3) | -0.005 (3) | 0.004 (2) | -0.004 (2) |
| C7 | 0.041 (2) | 0.039 (2) | 0.046 (2) | -0.0097 (18) | 0.0084 (19) | -0.0049 (19) |
| C8 | 0.074 (4) | 0.034 (3) | 0.104 (4) | 0.002 (2) | 0.043 (3) | -0.012 (3) |
| C9 | 0.070 (3) | 0.042 (3) | 0.088 (4) | -0.012 (3) | 0.036 (3) | -0.004 (3) |
| C10 | 0.041 (2) | 0.050 (3) | 0.046 (2) | -0.003 (2) | 0.0061 (19) | -0.010 (2) |
| C11 | 0.053 (3) | 0.048 (3) | 0.056 (2) | 0.014 (2) | 0.009 (2) | 0.006 (2) |
| C12 | 0.047 (3) | 0.046 (2) | 0.048 (2) | 0.008 (2) | 0.009 (2) | 0.009 (2) |
| C13 | 0.069 (4) | 0.076 (4) | 0.061 (3) | -0.009 (3) | 0.022 (3) | -0.005 (3) |
| N1 | 0.045 (2) | 0.047 (2) | 0.0491 (19) | -0.0044 (17) | -0.0041 (17) | -0.0074 (18) |
| O1 | 0.054 (2) | 0.063 (2) | 0.0671 (19) | 0.0007 (18) | 0.0269 (18) | 0.0025 (18) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|--------------------|-----------|------------|-----------|
| C1—N1 | 1.344 (6) | C7—C8 | 1.391 (6) |
| C1—C2 | 1.366 (7) | C8—C9 | 1.389 (6) |
| C1—H1 | 0.9300 | C8—H8 | 0.9300 |
| C2—C3 | 1.380 (6) | C9—C10 | 1.357 (6) |
| C2—H2 | 0.9300 | C9—H9 | 0.9300 |
| C3—C4 | 1.381 (6) | C10—C11 | 1.368 (6) |
| C3—H3 | 0.9300 | C10—O1 | 1.384 (5) |
| C4—C5 | 1.386 (6) | C11—C12 | 1.384 (6) |
| C4—C6 | 1.540 (5) | C11—H11 | 0.9300 |
| C5—N1 | 1.336 (5) | C12—H12 | 0.9300 |
| C5—C5 ⁱ | 1.458 (8) | C13—O1 | 1.401 (5) |
| C6—C7 | 1.528 (5) | C13—H13A | 0.9600 |
| C6—C7 ⁱ | 1.528 (5) | C13—H13B | 0.9600 |
| C6—C4 ⁱ | 1.540 (5) | C13—H13C | 0.9600 |
| C7—C12 | 1.379 (5) | | |
| N1—C1—C2 | 124.1 (4) | C9—C8—C7 | 121.9 (5) |
| N1—C1—H1 | 118.0 | C9—C8—H8 | 119.0 |
| C2—C1—H1 | 118.0 | C7—C8—H8 | 119.0 |
| C1—C2—C3 | 120.0 (4) | C10—C9—C8 | 119.7 (5) |
| C1—C2—H2 | 120.0 | C10—C9—H9 | 120.1 |
| C3—C2—H2 | 120.0 | C8—C9—H9 | 120.1 |
| C2—C3—C4 | 117.7 (4) | C9—C10—C11 | 119.8 (4) |

| | | | |
|-------------------------------------|------------|---------------------------|------------|
| C2—C3—H3 | 121.2 | C9—C10—O1 | 125.1 (4) |
| C4—C3—H3 | 121.2 | C11—C10—O1 | 115.1 (4) |
| C3—C4—C5 | 118.1 (4) | C10—C11—C12 | 120.3 (4) |
| C3—C4—C6 | 130.3 (4) | C10—C11—H11 | 119.9 |
| C5—C4—C6 | 111.6 (3) | C12—C11—H11 | 119.9 |
| N1—C5—C4 | 125.3 (4) | C7—C12—C11 | 121.7 (4) |
| N1—C5—C5 ⁱ | 126.0 (2) | C7—C12—H12 | 119.1 |
| C4—C5—C5 ⁱ | 108.7 (2) | C11—C12—H12 | 119.1 |
| C7—C6—C7 ⁱ | 112.5 (5) | O1—C13—H13A | 109.5 |
| C7—C6—C4 ⁱ | 113.4 (2) | O1—C13—H13B | 109.5 |
| C7 ⁱ —C6—C4 ⁱ | 108.8 (2) | H13A—C13—H13B | 109.5 |
| C7—C6—C4 | 108.8 (2) | O1—C13—H13C | 109.5 |
| C7 ⁱ —C6—C4 | 113.4 (2) | H13A—C13—H13C | 109.5 |
| C4 ⁱ —C6—C4 | 99.3 (4) | H13B—C13—H13C | 109.5 |
| C12—C7—C8 | 116.5 (4) | C5—N1—C1 | 114.9 (4) |
| C12—C7—C6 | 122.9 (4) | C10—O1—C13 | 117.9 (4) |
| C8—C7—C6 | 120.3 (4) | | |
| N1—C1—C2—C3 | -0.2 (7) | C4 ⁱ —C6—C7—C8 | 171.8 (4) |
| C1—C2—C3—C4 | -0.3 (6) | C4—C6—C7—C8 | -78.7 (5) |
| C2—C3—C4—C5 | 0.8 (6) | C12—C7—C8—C9 | 0.3 (8) |
| C2—C3—C4—C6 | -177.8 (4) | C6—C7—C8—C9 | 174.1 (4) |
| C3—C4—C5—N1 | -0.8 (6) | C7—C8—C9—C10 | 1.8 (8) |
| C6—C4—C5—N1 | 178.0 (3) | C8—C9—C10—C11 | -2.5 (8) |
| C3—C4—C5—C5 ⁱ | -180.0 (4) | C8—C9—C10—O1 | 178.3 (4) |
| C6—C4—C5—C5 ⁱ | -1.2 (5) | C9—C10—C11—C12 | 1.2 (7) |
| C3—C4—C6—C7 | 60.3 (5) | O1—C10—C11—C12 | -179.6 (4) |
| C5—C4—C6—C7 | -118.3 (4) | C8—C7—C12—C11 | -1.8 (7) |
| C3—C4—C6—C7 ⁱ | -65.7 (5) | C6—C7—C12—C11 | -175.4 (4) |
| C5—C4—C6—C7 ⁱ | 115.7 (4) | C10—C11—C12—C7 | 1.1 (7) |
| C3—C4—C6—C4 ⁱ | 179.1 (5) | C4—C5—N1—C1 | 0.3 (6) |
| C5—C4—C6—C4 ⁱ | 0.5 (2) | C5 ⁱ —C5—N1—C1 | 179.4 (5) |
| C7 ⁱ —C6—C7—C12 | -138.8 (5) | C2—C1—N1—C5 | 0.2 (6) |
| C4 ⁱ —C6—C7—C12 | -14.8 (6) | C9—C10—O1—C13 | 4.7 (7) |
| C4—C6—C7—C12 | 94.7 (4) | C11—C10—O1—C13 | -174.5 (4) |
| C7 ⁱ —C6—C7—C8 | 47.8 (4) | | |

Symmetry codes: (i) $y, x, -z+1$.

Fig. 1

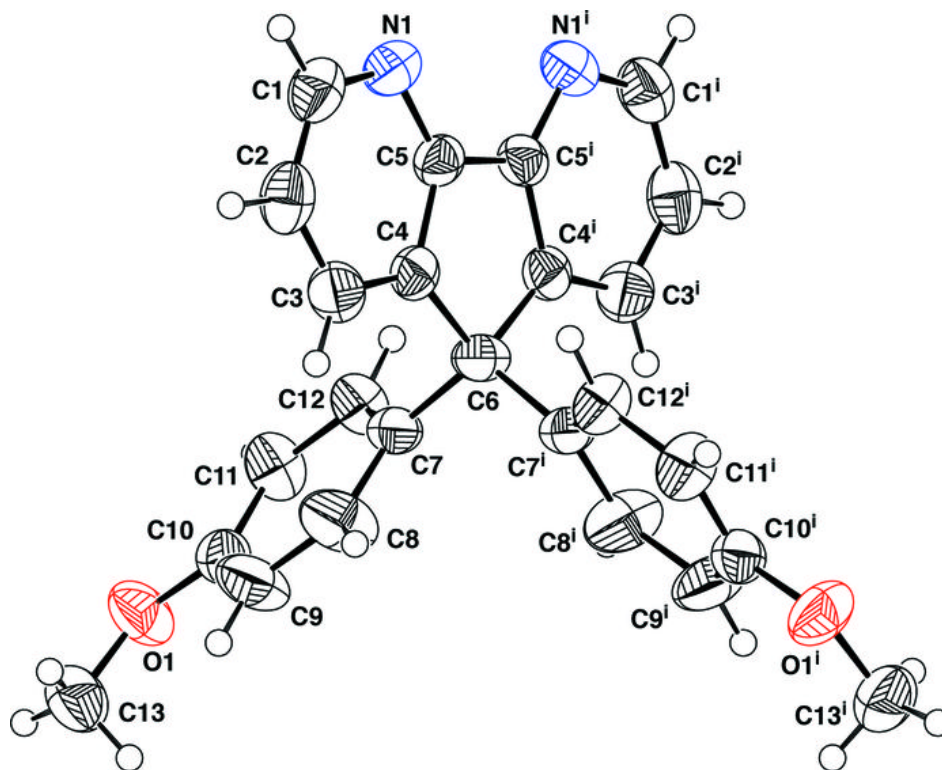


Fig. 2

