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Bis(1-tosyl-2-pyrrolyl)ethyne

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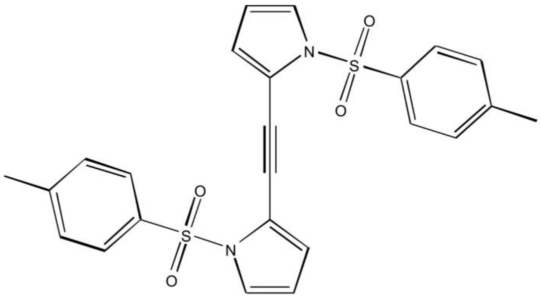
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.100; data-to-parameter ratio = 24.3.

The title molecule, $C_{24}H_{20}N_2O_4S_2$, has crystallographic inversion symmetry with a triple-bond distance of 1.206 (2) Å. The alkyne is not quite linear, with a C—C≡C angle of 175.78 (16)°. The planar pyrrole rings are parallel but offset from coplanarity by 0.318 (1) Å. The conformation of the sulfonyl group with respect to the pyrrole ring is such that an O atom is nearly eclipsed with this ring, having an O—S—N—C torsion angle of 3.48 (11)°. C—H···O interactions [C···O 3.278 (2) Å, 136° about H] between pyrrole H and sulfonyl O atoms lead to the formation of ladder-like chains.

Related literature

For related structures, see Abell *et al.* (1998); Knight *et al.* (2003); Tanui *et al.* (2008). For related literature, see: Vogel (1996); Chinchilla & Najera (2007); Desiraju & Steiner (1999).



Experimental

Crystal data

$C_{24}H_{20}N_2O_4S_2$
M_r = 464.54
Monoclinic, $P2_1/c$
a = 8.5127 (15) Å
b = 16.822 (2) Å
c = 7.5311 (11) Å
β = 101.049 (7)°
V = 1058.5 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 90 K
0.35 × 0.30 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer (with Oxford Cryostream)
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.896, T_{max} = 0.966
16546 measured reflections
3565 independent reflections
2995 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.100
S = 1.05
3565 reflections
147 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O2^{i}	0.95	2.53	3.278 (2)	136

Symmetry code: (i) x, y, z + 1.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *HKL SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The purchase of the diffractometer was made possible by Grant No. LEQSF(1999–2000)-ENH-TR-13, administered by the Louisiana Board of Regents.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2223).

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supplementary materials

Acta Cryst. (2008). E**64**, o130 [**doi:10.1107/S1600536807062964**]

Bis(1-tosyl-2-pyrrolyl)ethyne

H. K. Tanui, F. R. Fronczek and **M. G. H. Vicente**

Comment

Bis(1-tosyl-pyrrol-2-yl)ethyne (I) is an important intermediate in the synthesis of porphyrin analogues containing a two-carbon interpyrrolic bridge such as in corrphycene (Vogel, 1996). Compound (I) was prepared by an improved Sonogashira coupling reaction (Chinchilla & Najera, 2007) between 2-bromo-1-tosyl-pyrrole and ethyne-trimethylsilane in the presence of Pd(0) and Cu(I) catalysts at room temperature, see Experimental.

The molecule lies about an inversion center. The pyrrole rings are experimentally planar, but offset 0.318 (1) Å from co-planarity, because of the deviation from linearity of the C—C≡C—C group. Pyrrole-H atoms form intermolecular C—H···O interactions (Desiraju & Steiner, 1999) with sulfonate-O, C···O 3.278 (2) Å and angle of 136° about H. Thes einteractions lead to the formation of ladder-like chains along the [001] direction, Fig. 2.

The structures of related tosylpyrroles, *i.e.* 2-bromo-*N*-(*p*-toluenesulfonyl)pyrrole (Abell *et al.*, 1998) and 2-chloromethyl-1-(4-methylphenylsulfonyl)pyrrole (Knight *et al.*, 2003) have been reported. A similar compound containing the bis(2-pyrrolyl)ethyne core (Tanui *et al.*, 2008) lies on a twofold axis rather than an inversion center, and has its pyrrole groups twisted by 40.49 (4)° from co-planarity.

Experimental

To a 50 ml round bottom flask was added 2-bromo-1-tosyl-pyrrole (0.3 g, 1 mmol) followed by $Pd(PPh)_2Cl_2$(0.042 g, 0.06 mmol) and CuI (0.038 g 0.2 mmol). The flask was sealed and placed in a dry ice bath under N_2. Trimethylsilanylethyne (0.072 ml, 0.5 mmol), DBU (0.9 ml, 6 mmol) and water (0.0072 ml, 40 molar equiv.) were dissolved in benzene (5 ml) and added to the reaction flask. After the mixture froze in a dry ice bath, the flask was evacuated and N_2 gas added. The resulting reaction mixture was allowed to warm slowly to room temperature and was stirred until complete disappearance of the starting material, by TLC. The reaction mixture was worked up by adding ethyl acetate (100 ml), and washing the organic layer three times with saline. The organic phase was dried over anhydrous sodium bicarbonate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography using hexane/ethyl acetate (5:1) for elution. The bispyrrole-ethyne (I) was obtained in 8.4% yield (0.0194 g) and recrystallized from dichloromethane to afford colorless crystals. ^{1}H NMR (250 MHz, $CDCl_3$, 293 K, δ): 7.9 (4*H*, B, CH), 7.4 (4*H*, B, CH), 7.3 (2*H*, B, CH), 6.7 (2*H*, B, CH), 6.3 (2*H*, B, CH), 2.4 (6*H*, S, CH_3). MS (EI) m/*z*: 465.0939 (M^+). M·P.: 459 K.

Refinement

H atoms were placed in idealized positions with C—H distances 0.95–0.98 Å and thereafter treated as riding. U_{iso} for H was assigned as 1.2xU_{eq} of the attached C atoms (1.5 for methyl). A torsional parameter was refined for the methyl group.

Figures

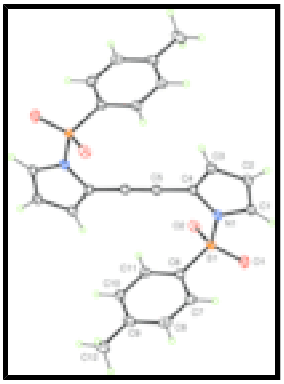

Fig. 1. Molecular structure of (I) showing displacement ellipsoids at the 50% level and H atoms having arbitrary radius. Unlabelled atoms are related by symmetry operation: 1 − *x*, 1 − *y*, 1 − *z*.

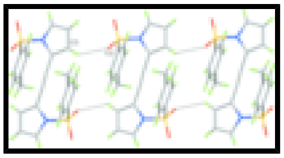

Fig. 2. View approximately down the *b* axis of the supramolecular chain in (I), showing C—H···O interactions as dashed lines.

Bis(1-tosyl-2-pyrrolyl)ethyne

Crystal data

$C_{24}H_{20}N_2O_4S_2$

M_r = 464.54

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

a = 8.5127 (15) Å

b = 16.822 (2) Å

c = 7.5311 (11) Å

β = 101.049 (7)°

V = 1058.5 (3) Å^3

Z = 2

F_{000} = 484

D_x = 1.458 Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3246 reflections

θ = 2.5–32.5°

μ = 0.29 mm^{-1}

T = 90 K

Fragment, colorless

0.35 × 0.30 × 0.12 mm

Data collection

Nonius KappaCCD (with Oxford Cryostream) diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 90 K

ω scans with κ offsets

Absorption correction: multi-scan
(HKL SCALEPACK; Otwinowski & Minor 1997)

T_{min} = 0.896, T_{max} = 0.966

16546 measured reflections

3565 independent reflections

2995 reflections with $I > 2\sigma(I)$

R_{int} = 0.019

θ_{max} = 32.6°

θ_{min} = 2.7°

h = −12→12

k = −20→24

l = −11→11

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.5421P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
3565 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}
147 parameters	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0087 (19)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.17966 (3)	0.588570 (17)	0.18361 (4)	0.01389 (9)
O1	0.03490 (11)	0.62987 (6)	0.10845 (12)	0.0205 (2)
O2	0.21216 (11)	0.51113 (5)	0.12117 (12)	0.01826 (19)
N1	0.17450 (12)	0.58026 (6)	0.40533 (13)	0.01363 (19)
C1	0.04720 (14)	0.60559 (7)	0.48222 (16)	0.0155 (2)
H1	−0.0438	0.6342	0.4222	0.019*
C2	0.07578 (14)	0.58208 (7)	0.65906 (16)	0.0159 (2)
H2	0.0083	0.5915	0.7437	0.019*
C3	0.22451 (15)	0.54103 (7)	0.69389 (15)	0.0154 (2)
H3	0.2736	0.5181	0.8061	0.018*
C4	0.28522 (14)	0.54024 (7)	0.53683 (15)	0.0135 (2)
C5	0.43438 (14)	0.51145 (7)	0.50710 (15)	0.0143 (2)
C6	0.34514 (14)	0.64976 (7)	0.17831 (15)	0.0141 (2)
C7	0.33400 (15)	0.73131 (7)	0.20914 (16)	0.0169 (2)
H7	0.2372	0.7541	0.2306	0.020*
C8	0.46788 (16)	0.77829 (7)	0.20758 (17)	0.0187 (2)

H8	0.4622	0.8338	0.2286	0.022*
C9	0.61100 (15)	0.74548 (8)	0.17564 (16)	0.0183 (2)
C10	0.61811 (15)	0.66412 (8)	0.14272 (16)	0.0172 (2)
H10	0.7143	0.6414	0.1193	0.021*
C11	0.48522 (14)	0.61580 (7)	0.14388 (15)	0.0151 (2)
H11	0.4903	0.5604	0.1214	0.018*
C12	0.75453 (18)	0.79796 (9)	0.1772 (2)	0.0262 (3)
H12A	0.8386	0.7676	0.1351	0.039*
H12B	0.7946	0.8170	0.3005	0.039*
H12C	0.7238	0.8435	0.0968	0.039*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01179 (14)	0.01874 (15)	0.01119 (13)	−0.00136 (10)	0.00237 (9)	0.00013 (9)
O1	0.0125 (4)	0.0318 (5)	0.0161 (4)	0.0012 (4)	0.0001 (3)	0.0038 (4)
O2	0.0202 (4)	0.0203 (4)	0.0152 (4)	−0.0047 (3)	0.0056 (3)	−0.0036 (3)
N1	0.0112 (4)	0.0182 (5)	0.0119 (4)	0.0008 (3)	0.0032 (3)	0.0007 (3)
C1	0.0121 (5)	0.0191 (5)	0.0164 (5)	0.0016 (4)	0.0051 (4)	0.0000 (4)
C2	0.0140 (5)	0.0188 (5)	0.0160 (5)	0.0004 (4)	0.0060 (4)	−0.0012 (4)
C3	0.0150 (5)	0.0186 (5)	0.0136 (5)	0.0005 (4)	0.0051 (4)	0.0003 (4)
C4	0.0123 (5)	0.0160 (5)	0.0122 (5)	0.0006 (4)	0.0028 (4)	0.0000 (4)
C5	0.0141 (5)	0.0173 (5)	0.0118 (4)	0.0001 (4)	0.0032 (4)	0.0012 (4)
C6	0.0133 (5)	0.0174 (5)	0.0117 (5)	−0.0011 (4)	0.0028 (4)	0.0017 (4)
C7	0.0178 (5)	0.0179 (5)	0.0151 (5)	0.0020 (4)	0.0029 (4)	0.0012 (4)
C8	0.0239 (6)	0.0159 (5)	0.0159 (5)	−0.0012 (4)	0.0030 (4)	0.0015 (4)
C9	0.0185 (6)	0.0211 (6)	0.0146 (5)	−0.0052 (4)	0.0017 (4)	0.0034 (4)
C10	0.0138 (5)	0.0214 (6)	0.0166 (5)	−0.0004 (4)	0.0038 (4)	0.0037 (4)
C11	0.0154 (5)	0.0161 (5)	0.0141 (5)	0.0003 (4)	0.0039 (4)	0.0017 (4)
C12	0.0254 (7)	0.0283 (7)	0.0256 (6)	−0.0114 (5)	0.0062 (5)	0.0019 (5)

Geometric parameters (Å, °)

S1—O2	1.4298 (10)	C6—C11	1.3907 (17)
S1—O1	1.4333 (10)	C6—C7	1.3977 (17)
S1—N1	1.6845 (10)	C7—C8	1.3888 (18)
S1—C6	1.7513 (12)	C7—H7	0.9500
N1—C1	1.3900 (15)	C8—C9	1.3997 (19)
N1—C4	1.4016 (15)	C8—H8	0.9500
C1—C2	1.3656 (17)	C9—C10	1.3945 (18)
C1—H1	0.9500	C9—C12	1.5056 (18)
C2—C3	1.4218 (17)	C10—C11	1.3944 (17)
C2—H2	0.9500	C10—H10	0.9500
C3—C4	1.3786 (16)	C11—H11	0.9500
C3—H3	0.9500	C12—H12A	0.9800
C4—C5	1.4164 (16)	C12—H12B	0.9800
C5—C5^{i}	1.206 (2)	C12—H12C	0.9800
O2—S1—O1	121.17 (6)	C11—C6—S1	119.01 (9)

O2—S1—N1	107.09 (5)	C7—C6—S1	119.51 (9)
O1—S1—N1	104.35 (5)	C8—C7—C6	118.37 (11)
O2—S1—C6	108.71 (6)	C8—C7—H7	120.8
O1—S1—C6	109.91 (6)	C6—C7—H7	120.8
N1—S1—C6	104.20 (5)	C7—C8—C9	121.32 (12)
C1—N1—C4	108.98 (9)	C7—C8—H8	119.3
C1—N1—S1	123.92 (8)	C9—C8—H8	119.3
C4—N1—S1	126.76 (8)	C10—C9—C8	119.11 (11)
C2—C1—N1	108.07 (10)	C10—C9—C12	120.93 (12)
C2—C1—H1	126.0	C8—C9—C12	119.96 (12)
N1—C1—H1	126.0	C11—C10—C9	120.54 (12)
C1—C2—C3	107.85 (10)	C11—C10—H10	119.7
C1—C2—H2	126.1	C9—C10—H10	119.7
C3—C2—H2	126.1	C6—C11—C10	119.17 (11)
C4—C3—C2	108.26 (10)	C6—C11—H11	120.4
C4—C3—H3	125.9	C10—C11—H11	120.4
C2—C3—H3	125.9	C9—C12—H12A	109.5
C3—C4—N1	106.85 (10)	C9—C12—H12B	109.5
C3—C4—C5	129.33 (11)	H12A—C12—H12B	109.5
N1—C4—C5	123.67 (10)	C9—C12—H12C	109.5
C5$^{\mathrm{i}}$—C5—C4	175.78 (16)	H12A—C12—H12C	109.5
C11—C6—C7	121.47 (11)	H12B—C12—H12C	109.5

O2—S1—N1—C1	−126.14 (10)	O2—S1—C6—C11	−9.04 (11)
O1—S1—N1—C1	3.48 (11)	O1—S1—C6—C11	−143.78 (9)
C6—S1—N1—C1	118.78 (10)	N1—S1—C6—C11	104.90 (10)
O2—S1—N1—C4	46.48 (11)	O2—S1—C6—C7	171.15 (9)
O1—S1—N1—C4	176.09 (10)	O1—S1—C6—C7	36.41 (11)
C6—S1—N1—C4	−68.61 (11)	N1—S1—C6—C7	−74.92 (10)
C4—N1—C1—C2	−0.14 (13)	C11—C6—C7—C8	−1.01 (17)
S1—N1—C1—C2	173.61 (9)	S1—C6—C7—C8	178.80 (9)
N1—C1—C2—C3	−0.01 (14)	C6—C7—C8—C9	0.15 (18)
C1—C2—C3—C4	0.16 (14)	C7—C8—C9—C10	0.76 (18)
C2—C3—C4—N1	−0.24 (13)	C7—C8—C9—C12	−179.25 (12)
C2—C3—C4—C5	175.18 (12)	C8—C9—C10—C11	−0.83 (18)
C1—N1—C4—C3	0.23 (13)	C12—C9—C10—C11	179.17 (11)
S1—N1—C4—C3	−173.29 (9)	C7—C6—C11—C10	0.93 (17)
C1—N1—C4—C5	−175.51 (11)	S1—C6—C11—C10	−178.88 (9)
S1—N1—C4—C5	10.97 (17)	C9—C10—C11—C6	0.01 (17)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O2$^{\mathrm{ii}}$	0.95	2.53	3.278 (2)	136

Symmetry codes: (ii) *x*, *y*, *z*+1.

Fig. 1

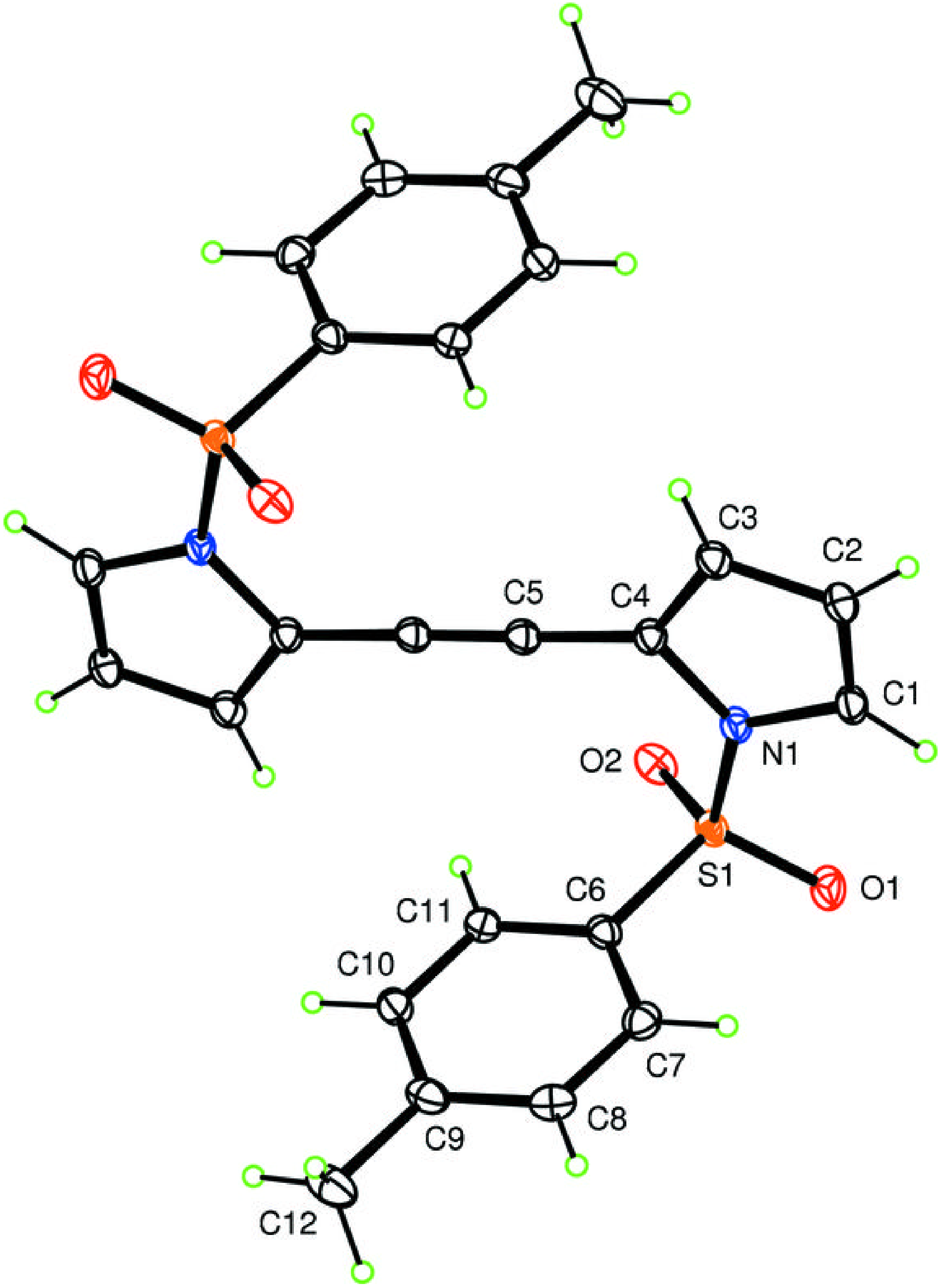

Fig. 2