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2-[[**(Biphenyl-2-yl)diazenyl**]methylidene]-1,3,3-trimethylindoline

Graeme J. Gainsford,\* Mohamed Ashraf and Andrew J. Kay

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand

Correspondence e-mail: g.gainsford@irl.cri.nz

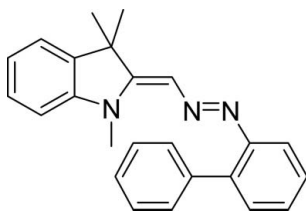
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Key indicators: single-crystal X-ray study;  $T = 116$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.086; data-to-parameter ratio = 7.2.

The title molecule,  $\text{C}_{24}\text{H}_{23}\text{N}_3$ , shows some delocalization of charge based on the small  $[8.0(2)^\circ]$  angle between the indolin-2-ylidene ring system and the link methylidiazene  $\text{C}_2\text{N}_2$  atom plane. A further twist of  $17.2(3)^\circ$  is subtended between the  $\text{C}_2\text{N}_2$  plane and its attached benzene ring. The dihedral angle between the biphenyl rings is  $47.96(14)^\circ$ . In the crystal, the molecules pack *via*  $\text{C}-\text{H}\cdots\pi$  attractive interactions.

## Related literature

For applications of azo compounds, see: Möhlmann & van der Vorst (1989); Zollinger (1987). For related compounds, see Jones (2004); Jones & Chrapkowski (2004); Gainsford *et al.* (2008). For a description of the Cambridge Structural Database, see: Allen (2002).



## Experimental

## Crystal data

 $\text{C}_{24}\text{H}_{23}\text{N}_3$  $M_r = 353.45$ Orthorhombic,  $Pca2_1$  $a = 14.2968(17)$  Å $b = 8.2407(10)$  Å $c = 16.2671(17)$  Å $V = 1916.5(4)$  Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.07$  mm<sup>-1</sup> $T = 116$  K $0.70 \times 0.20 \times 0.10$  mm

## Data collection

Bruker APEXII CCD diffractometer

Absorption correction: multi-scan [Blessing (1995) and SADABS (Bruker, 2005)]

 $T_{\min} = 0.640$ ,  $T_{\max} = 0.746$ 

34258 measured reflections

1783 independent reflections

1764 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.041$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.037$  $wR(F^2) = 0.086$  $S = 1.23$ 

1783 reflections

247 parameters

1 restraint

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.19$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.16$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$\text{Cg1}$ ,  $\text{Cg2}$  and  $\text{Cg3}$  are the centroids of the  $\text{C19}-\text{C24}$ ,  $\text{C4}-\text{C9}$  and  $\text{C13}-\text{C18}$  rings, respectively.

| $D-\text{H}\cdots A$                          | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|---|--------------|--------------------|-------------|----------------------|
| $\text{C1}-\text{H1C}\cdots\text{Cg1}^i$      | 0.98         | 2.86               | 3.582 (3)   | 131                  |
| $\text{C11}-\text{H11B}\cdots\text{Cg3}^{ii}$ | 0.98         | 2.74               | 3.721 (3)   | 179                  |
| $\text{C22}-\text{H22}\cdots\text{Cg2}^{iii}$ | 0.95         | 2.76               | 3.645 (3)   | 155                  |

Symmetry codes: (i)  $x + \frac{1}{2}, -y + 2, z$ ; (ii)  $x + \frac{1}{2}, -y + 1, z$ ; (iii)  $-x + 1, -y + 2, z - \frac{1}{2}$ .

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2009).

We thank Dr J. Wikaira of the University of Canterbury, New Zealand, for her assistance with the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: EZ2238).

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**supplementary materials**

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## 2-{{(Biphenyl-2-yl)diazenyl}methylidene}-1,3,3-trimethylindoline

G. J. Gainsford, M. Ashraf and A. J. Kay

### Comment

Azo compounds are integral to a number of fields of organic chemistry. While they played a key part in the development of the dye industry (Zollinger, 1987) they are also finding application as the enabling materials for a range of fields including nonlinear optics, photochromism and holographic recording. Dyes based on azobenzene typically exhibit high extinction coefficients and their absorption maxima can usually be tailored to lie anywhere in the visible region *via* appropriate substitution onto the phenyl rings. Furthermore due to their geometrically rigid structures and large aspect ratios, azobenzene compounds are ideal as mesogens (Möhlmann & van der Vorst, 1989).

Recently, we have become interested in developing photoswitchable molecules in order to alter the refractive index of a given material *via* photo-induced rather than electrically induced means (as occurs in nonlinear optical materials). As part of this we have been exploring how the placement of different substituents (*e.g.* donors, acceptors or neutral) on the backbone of various azo dyes affects the speed and reversibility of the photo- and thermal isomerization processes. Included in these studies have been a suite of compounds containing an indoline donor, an azo linker and a variety of substituents attached to the terminal nitrogen atom of the azo moiety. The molecules are easily prepared *via* diazotization of the corresponding aryl amine of the terminal substituent and coupling of the resultant diazonium salt with Fisher's base. The reaction is exemplified in Fig. 1 using 2-aminobiphenyl, **1**, as the aromatic amine and which yielded the title compound, **3**, in 80% yield.

Compound REFCODES below are from the Cambridge Structural Database (Version 5.31, with Aug 2010 updates; Allen, 2002). The asymmetric unit contents and labels of **3** are shown in Fig. 2. The bond lengths and angles, with the exception of those involving atom C12, are essentially identical with those reported by Jones in 2004 [EZUCUX, EZUDAE (Jones, 2004)] and YADTIH (Jones & Chrapkowski (2004)]. In these latter three compounds, where only a phenyl (or *para*-substituted phenyl) ring was bound to N3, an additional indol-2-ylidene ring was bonded to C12 rather than the hydrogen here (H12). The mean C12—C2 and C12—N2 distances for the three structures were 1.386 (5) and 1.395 (2) Å compared with 1.361 (4) and 1.362 (4) Å here. There are smaller consistent, but barely significant, differences with the N1—C9 and N1—C2 average bond lengths being longer (0.11 (5) Å) and shorter (0.08 (5) °) than found here. These differences can be attributed to extended charge delocalization through the N1—C2—C12—N2 chain that is not observed in the three reference cationic structures.

There is minor buckling between the 5- & 6-membered rings in the indol-2-ylidene ring of 1.09 (14) ° compared with 0.46 (14) ° in EZUDAE. The interplanar angles confirm the consistent twist along the delocalization plane: 8.0 (2) ° between the indol-2-ylidene (N1, C2—C9) and the C2,C12,N2,N3 planes, and a further 17.2 (3) ° angle subtended between the latter and the phenyl ring (C14—C18). The biphenyl rings are at 47.96 (14) ° to each other. This is another point of difference with the related compounds, where the "out of plane" indol-2-ylidene ring bound to C12 is at ~80 ° to the mean plane through the phenyl ring bound to N3.

The molecules are held in the lattice by a concerted set of C—H... $\pi$  interactions shown in Table 1 and Fig. 3. Entry 2 in Table 1 is included because the second methyl hydrogen on C1 (H1A) interacts with atoms C14 & C15 in an adjacent (*Cg*3)

## supplementary materials

ring. We note that the acidic proton H12 is not positioned to interact with adjacent N2 or N3 acceptors as observed in related compounds with cyano N atoms (*e.g.* structure (II) in Gainsford *et al.*, 2008). This packing highlights the main difference between this structure and the reference compounds which have extensive hydrogen bonding (C—H $\cdots$ O) to the perchlorate anion and no significant C—H $\cdots$  $\pi$  interactions.

### Experimental

To conc. sulfuric acid (4 ml) was added 2-aminobiphenyl **1** (5 mmol) and the reaction was stirred and cooled to 273–278 K. A solution of sodium nitrite (380 mg, 5.5 mol) in 10 ml of water was added slowly and the reaction stirred at 273–278 K for 30 min. To this mixture, was added a solution of Fisher's base, **2**, (865 mg, 5 mmol) in 20 ml of glacial acetic acid and the reaction was then stirred for a further 2 h at 273–278 K. The reaction mixture was then poured into water and neutralized with aqueous sodium carbonate. The resulting precipitate was collected by filtration, washed with water and dried over sodium sulfate. Recrystallization (ethanol) gave the title compound **3** as a deep red solid; Yield: 80%. Crystals were prepared by slow evaporation in methanol. m.p. 417.8–419.3 K.  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz): 7.58 (d, 1H,  $J = 10$  Hz), 7.46–7.40 (m, 5H), 7.35–7.31 (m, 2H), 7.29–7.25 (m, 2H), 7.22 (s, 1H), 7.09 (d, 1H,  $J = 10$  Hz), 7.02 (t, 2H), 3.31(s, 3H), 1.71(s, 6H).  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz): 28.66, 29.58, 108.23, 115.62, 121.61, 121.87, 126.58, 126.99, 127.54, 127.81, 128.05, 130.30, 131.53, 137.72, 139.35, 139.70, 144.08, 150.79, 165.97. Mass spec: found:  $M^+$  354.1972; 354.1970 (calc);  $\Delta = 0.6$  p.p.m..

### Refinement

In the absence of significant anomalous scattering, the values of the Flack parameter were indeterminate. Accordingly, the Friedel-equivalent reflections were merged prior to the final refinements. Two reflections affected by the backstop were omitted from the refinements (using *OMIT*) and three others were deemed to be outliers. The methyl H atoms were constrained to an ideal geometry (C—H = 0.98 Å) with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ , but were allowed to rotate freely about the adjacent C—C bond. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances of 1.00 (primary), 0.99 (methylene) or 0.95 (phenyl) Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Figures

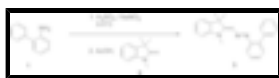


Fig. 1. Reaction scheme showing the synthetic procedure for obtaining the title compound.

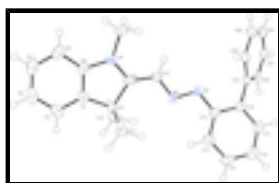


Fig. 2. Molecular structure of the asymmetric unit (Farrugia, 1997); displacement ellipsoids are shown at the 50% probability level. H atoms not shown for clarity.

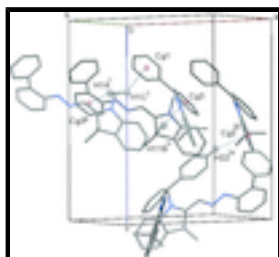


Fig. 3. Partial packing diagram of the unit cell showing key interactions (see text and Table 1) [Macrae *et al.*, 2008]. Only significant H atoms are shown as balls for clarity. Symmetry (i)  $x - 1/2, 2 - y, z$  (ii)  $1/2 - x, 1 - y, z$  (iii)  $x, y - 1, z$  (iv)  $1 - x, 1 - y, 1/2 + z$  (v)  $x - 1/2, 1 - y, z$ . Ring centres shown as red balls are Cg1 (C19–C24), Cg2 (C4–C9) and Cg3 (C13–C18).

2-[[**(Biphenyl-2-yl)diazenyl**]methylidene]-1,3,3-trimethylindoline

*Crystal data*

|                                |   |
|--------------------------------|---|
| $C_{24}H_{23}N_3$              | $F(000) = 752$  |
| $M_r = 353.45$                 | $D_x = 1.225 \text{ Mg m}^{-3}$                         |
| Orthorhombic, $Pca2_1$         | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| Hall symbol: P 2c -2ac         | Cell parameters from 9914 reflections                   |
| $a = 14.2968 (17) \text{ \AA}$ | $\theta = 2.5\text{--}27.3^\circ$                       |
| $b = 8.2407 (10) \text{ \AA}$  | $\mu = 0.07 \text{ mm}^{-1}$                            |
| $c = 16.2671 (17) \text{ \AA}$ | $T = 116 \text{ K}$                                     |
| $V = 1916.5 (4) \text{ \AA}^3$ | Needle, red   |
| $Z = 4$                        | $0.70 \times 0.20 \times 0.10 \text{ mm}$               |

*Data collection*

|  |  |
|--|--|
| Bruker APEXII CCD diffractometer   | 1783 independent reflections   |
| graphite   | 1764 reflections with $I > 2\sigma(I)$                                 |
| Detector resolution: $8.333 \text{ pixels mm}^{-1}$                                  | $R_{\text{int}} = 0.041$   |
| $\varphi$ and $\omega$ scans   | $\theta_{\text{max}} = 25.2^\circ$ , $\theta_{\text{min}} = 2.5^\circ$ |
| Absorption correction: multi-scan [Blessing (1995) and <i>SADABS</i> (Bruker, 2005)] | $h = -17 \rightarrow 17$   |
| $T_{\text{min}} = 0.640$ , $T_{\text{max}} = 0.746$                                  | $k = -9 \rightarrow 9$   |
| 34258 measured reflections   | $l = -19 \rightarrow 19$   |

*Refinement*

|                                 |  |
|---------------------------------|--|
| Refinement on $F^2$             | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full      | Secondary atom site location: difference Fourier map           |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | Hydrogen site location: inferred from neighbouring sites       |
| $wR(F^2) = 0.086$               | H-atom parameters constrained                                  |
| $S = 1.23$                      | $w = 1/[\sigma^2(F_o^2) + (0.0282P)^2 + 0.7948P]$              |
| 1783 reflections                | where $P = (F_o^2 + 2F_c^2)/3$                                 |
| 247 parameters                  | $(\Delta/\sigma)_{\text{max}} < 0.001$                         |
| 1 restraint                     | $\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$            |
|                                 | $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$           |

*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.

## supplementary materials

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

|      | $x$          | $y$        | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|------------|--------------|----------------------------------|
| N1   | 0.78152 (16) | 1.0321 (3) | 0.45002 (13) | 0.0248 (5)                       |
| N2   | 0.64108 (16) | 0.6649 (3) | 0.43989 (14) | 0.0238 (5)                       |
| N3   | 0.58268 (16) | 0.6112 (3) | 0.38682 (14) | 0.0261 (5)                       |
| C1   | 0.7761 (2)   | 1.1095 (4) | 0.36962 (19) | 0.0333 (7)                       |
| H1A  | 0.7164       | 1.1669     | 0.3645       | 0.050*                           |
| H1B  | 0.7806       | 1.0267     | 0.3266       | 0.050*                           |
| H1C  | 0.8277       | 1.1869     | 0.3637       | 0.050*                           |
| C2   | 0.73892 (18) | 0.8894 (3) | 0.47008 (16) | 0.0216 (6)                       |
| C3   | 0.76949 (18) | 0.8406 (3) | 0.55730 (17) | 0.0235 (6)                       |
| C4   | 0.83106 (18) | 0.9831 (3) | 0.58035 (17) | 0.0250 (6)                       |
| C5   | 0.8798 (2)   | 1.0170 (4) | 0.6516 (2)   | 0.0376 (7)                       |
| H5   | 0.8786       | 0.9433     | 0.6965       | 0.045*                           |
| C6   | 0.9309 (2)   | 1.1616 (4) | 0.6568 (2)   | 0.0444 (9)                       |
| H6   | 0.9645       | 1.1863     | 0.7056       | 0.053*                           |
| C7   | 0.9329 (2)   | 1.2686 (4) | 0.5914 (2)   | 0.0421 (8)                       |
| H7   | 0.9679       | 1.3663     | 0.5962       | 0.050*                           |
| C8   | 0.8851 (2)   | 1.2369 (4) | 0.5189 (2)   | 0.0349 (7)                       |
| H8   | 0.8866       | 1.3101     | 0.4738       | 0.042*                           |
| C9   | 0.83496 (19) | 1.0929 (3) | 0.51568 (18) | 0.0258 (6)                       |
| C10  | 0.6853 (2)   | 0.8259 (4) | 0.61544 (18) | 0.0321 (7)                       |
| H10A | 0.6504       | 0.9283     | 0.6157       | 0.048*                           |
| H10B | 0.7073       | 0.8019     | 0.6712       | 0.048*                           |
| H10C | 0.6443       | 0.7381     | 0.5965       | 0.048*                           |
| C11  | 0.8248 (2)   | 0.6797 (3) | 0.55651 (19) | 0.0276 (6)                       |
| H11A | 0.8479       | 0.6563     | 0.6120       | 0.041*                           |
| H11B | 0.8778       | 0.6891     | 0.5187       | 0.041*                           |
| H11C | 0.7837       | 0.5914     | 0.5384       | 0.041*                           |
| C12  | 0.67785 (19) | 0.8119 (3) | 0.41935 (17) | 0.0245 (6)                       |
| H12  | 0.6606       | 0.8612     | 0.3688       | 0.029*                           |
| C13  | 0.55193 (18) | 0.4505 (3) | 0.40219 (17) | 0.0240 (6)                       |
| C14  | 0.5934 (2)   | 0.3493 (4) | 0.46096 (19) | 0.0312 (7)                       |
| H14  | 0.6403       | 0.3914     | 0.4964       | 0.037*                           |
| C15  | 0.5666 (2)   | 0.1883 (3) | 0.46788 (19) | 0.0316 (7)                       |
| H15  | 0.5948       | 0.1210     | 0.5083       | 0.038*                           |
| C16  | 0.4991 (2)   | 0.1253 (3) | 0.4164 (2)   | 0.0323 (7)                       |
| H16  | 0.4833       | 0.0135     | 0.4191       | 0.039*                           |
| C17  | 0.4546 (2)   | 0.2260 (3) | 0.36077 (18) | 0.0282 (6)                       |
| H17  | 0.4065       | 0.1826     | 0.3271       | 0.034*                           |
| C18  | 0.47830 (19) | 0.3887 (3) | 0.35274 (16) | 0.0245 (6)                       |
| C19  | 0.42423 (19) | 0.4918 (3) | 0.29410 (17) | 0.0247 (6)                       |

|     |              |            |              |            |
|-----|--------------|------------|--------------|------------|
| C20 | 0.32655 (19) | 0.4815 (3) | 0.29415 (18) | 0.0280 (6) |
| H20 | 0.2962       | 0.4128     | 0.3327       | 0.034*     |
| C21 | 0.2735 (2)   | 0.5700 (4) | 0.23883 (19) | 0.0336 (7) |
| H21 | 0.2073       | 0.5609     | 0.2397       | 0.040*     |
| C22 | 0.3156 (2)   | 0.6708 (4) | 0.1826 (2)   | 0.0371 (7) |
| H22 | 0.2789       | 0.7308     | 0.1446       | 0.045*     |
| C23 | 0.4127 (2)   | 0.6838 (4) | 0.18199 (19) | 0.0367 (8) |
| H23 | 0.4424       | 0.7541     | 0.1438       | 0.044*     |
| C24 | 0.4663 (2)   | 0.5949 (4) | 0.23681 (18) | 0.0304 (7) |
| H24 | 0.5325       | 0.6041     | 0.2354       | 0.036*     |

*Atomic displacement parameters ( $\text{\AA}^2$ )*

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$     | $U^{13}$     | $U^{23}$     |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| N1  | 0.0280 (12) | 0.0215 (11) | 0.0248 (12) | 0.0027 (9)   | 0.0003 (9)   | 0.0034 (10)  |
| N2  | 0.0218 (11) | 0.0250 (12) | 0.0247 (11) | 0.0029 (9)   | -0.0005 (9)  | -0.0013 (10) |
| N3  | 0.0282 (12) | 0.0252 (12) | 0.0248 (12) | 0.0016 (10)  | -0.0049 (10) | -0.0008 (10) |
| C1  | 0.0377 (16) | 0.0289 (15) | 0.0334 (16) | 0.0005 (13)  | 0.0023 (13)  | 0.0120 (14)  |
| C2  | 0.0218 (13) | 0.0214 (12) | 0.0216 (13) | 0.0049 (11)  | 0.0021 (11)  | 0.0014 (12)  |
| C3  | 0.0247 (14) | 0.0243 (13) | 0.0215 (13) | 0.0042 (11)  | -0.0006 (11) | 0.0012 (12)  |
| C4  | 0.0201 (13) | 0.0302 (15) | 0.0249 (13) | 0.0072 (11)  | 0.0024 (11)  | -0.0055 (12) |
| C5  | 0.0318 (16) | 0.0471 (18) | 0.0339 (16) | 0.0055 (14)  | -0.0057 (14) | -0.0054 (16) |
| C6  | 0.0334 (17) | 0.056 (2)   | 0.0438 (19) | 0.0024 (15)  | -0.0076 (15) | -0.0196 (18) |
| C7  | 0.0269 (16) | 0.0374 (18) | 0.062 (2)   | -0.0023 (14) | 0.0000 (15)  | -0.0175 (17) |
| C8  | 0.0273 (16) | 0.0272 (15) | 0.0502 (18) | 0.0014 (12)  | 0.0067 (14)  | -0.0066 (15) |
| C9  | 0.0210 (13) | 0.0241 (14) | 0.0324 (14) | 0.0034 (11)  | 0.0036 (12)  | -0.0065 (13) |
| C10 | 0.0287 (15) | 0.0413 (18) | 0.0264 (15) | 0.0042 (14)  | 0.0048 (12)  | 0.0063 (13)  |
| C11 | 0.0279 (14) | 0.0273 (14) | 0.0276 (14) | 0.0031 (12)  | -0.0016 (12) | 0.0065 (13)  |
| C12 | 0.0285 (14) | 0.0228 (14) | 0.0220 (13) | 0.0030 (11)  | -0.0004 (11) | 0.0031 (11)  |
| C13 | 0.0248 (14) | 0.0238 (13) | 0.0234 (13) | 0.0049 (11)  | 0.0057 (11)  | -0.0019 (11) |
| C14 | 0.0301 (15) | 0.0330 (16) | 0.0305 (15) | 0.0051 (12)  | 0.0007 (13)  | -0.0011 (13) |
| C15 | 0.0336 (16) | 0.0267 (15) | 0.0345 (16) | 0.0106 (12)  | 0.0096 (13)  | 0.0099 (14)  |
| C16 | 0.0336 (16) | 0.0243 (14) | 0.0391 (16) | 0.0006 (13)  | 0.0152 (13)  | 0.0016 (14)  |
| C17 | 0.0255 (14) | 0.0287 (15) | 0.0304 (15) | -0.0037 (12) | 0.0087 (12)  | -0.0015 (12) |
| C18 | 0.0254 (14) | 0.0269 (14) | 0.0211 (13) | 0.0014 (11)  | 0.0088 (11)  | -0.0003 (11) |
| C19 | 0.0286 (14) | 0.0238 (13) | 0.0217 (13) | -0.0018 (11) | 0.0002 (12)  | -0.0067 (12) |
| C20 | 0.0288 (15) | 0.0272 (15) | 0.0282 (14) | -0.0041 (12) | 0.0000 (13)  | -0.0076 (13) |
| C21 | 0.0303 (16) | 0.0348 (16) | 0.0356 (16) | 0.0009 (13)  | -0.0067 (13) | -0.0118 (14) |
| C22 | 0.0432 (18) | 0.0377 (17) | 0.0304 (16) | 0.0063 (15)  | -0.0137 (14) | -0.0030 (14) |
| C23 | 0.0448 (19) | 0.0423 (19) | 0.0230 (15) | -0.0037 (15) | -0.0044 (14) | 0.0070 (14)  |
| C24 | 0.0287 (15) | 0.0367 (17) | 0.0258 (14) | -0.0031 (13) | 0.0032 (12)  | -0.0005 (13) |

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

|        |           |          |           |
|--------|-----------|----------|-----------|
| N1—C2  | 1.364 (3) | C11—H11A | 0.9800    |
| N1—C9  | 1.405 (4) | C11—H11B | 0.9800    |
| N1—C1  | 1.457 (4) | C11—H11C | 0.9800    |
| N2—N3  | 1.280 (3) | C12—H12  | 0.9500    |
| N2—C12 | 1.362 (4) | C13—C14  | 1.400 (4) |

## supplementary materials

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|            |           |               |           |
|------------|-----------|---------------|-----------|
| N3—C13     | 1.418 (4) | C13—C18       | 1.419 (4) |
| C1—H1A     | 0.9800    | C14—C15       | 1.386 (4) |
| C1—H1B     | 0.9800    | C14—H14       | 0.9500    |
| C1—H1C     | 0.9800    | C15—C16       | 1.379 (5) |
| C2—C12     | 1.361 (4) | C15—H15       | 0.9500    |
| C2—C3      | 1.538 (4) | C16—C17       | 1.383 (4) |
| C3—C4      | 1.515 (4) | C16—H16       | 0.9500    |
| C3—C10     | 1.536 (4) | C17—C18       | 1.389 (4) |
| C3—C11     | 1.544 (4) | C17—H17       | 0.9500    |
| C4—C5      | 1.381 (4) | C18—C19       | 1.493 (4) |
| C4—C9      | 1.388 (4) | C19—C24       | 1.397 (4) |
| C5—C6      | 1.401 (5) | C19—C20       | 1.399 (4) |
| C5—H5      | 0.9500    | C20—C21       | 1.384 (4) |
| C6—C7      | 1.381 (5) | C20—H20       | 0.9500    |
| C6—H6      | 0.9500    | C21—C22       | 1.375 (5) |
| C7—C8      | 1.389 (5) | C21—H21       | 0.9500    |
| C7—H7      | 0.9500    | C22—C23       | 1.392 (5) |
| C8—C9      | 1.388 (4) | C22—H22       | 0.9500    |
| C8—H8      | 0.9500    | C23—C24       | 1.385 (4) |
| C10—H10A   | 0.9800    | C23—H23       | 0.9500    |
| C10—H10B   | 0.9800    | C24—H24       | 0.9500    |
| C10—H10C   | 0.9800    |               |           |
| C2—N1—C9   | 111.6 (2) | C3—C11—H11B   | 109.5     |
| C2—N1—C1   | 124.6 (2) | H11A—C11—H11B | 109.5     |
| C9—N1—C1   | 123.7 (2) | C3—C11—H11C   | 109.5     |
| N3—N2—C12  | 113.2 (2) | H11A—C11—H11C | 109.5     |
| N2—N3—C13  | 114.0 (2) | H11B—C11—H11C | 109.5     |
| N1—C1—H1A  | 109.5     | C2—C12—N2     | 121.1 (2) |
| N1—C1—H1B  | 109.5     | C2—C12—H12    | 119.5     |
| H1A—C1—H1B | 109.5     | N2—C12—H12    | 119.5     |
| N1—C1—H1C  | 109.5     | C14—C13—N3    | 123.0 (3) |
| H1A—C1—H1C | 109.5     | C14—C13—C18   | 119.2 (3) |
| H1B—C1—H1C | 109.5     | N3—C13—C18    | 117.7 (2) |
| C12—C2—N1  | 123.1 (2) | C15—C14—C13   | 120.6 (3) |
| C12—C2—C3  | 128.3 (2) | C15—C14—H14   | 119.7     |
| N1—C2—C3   | 108.6 (2) | C13—C14—H14   | 119.7     |
| C4—C3—C10  | 111.4 (2) | C16—C15—C14   | 120.3 (3) |
| C4—C3—C2   | 101.0 (2) | C16—C15—H15   | 119.8     |
| C10—C3—C2  | 111.5 (2) | C14—C15—H15   | 119.8     |
| C4—C3—C11  | 111.8 (2) | C15—C16—C17   | 119.6 (3) |
| C10—C3—C11 | 109.8 (2) | C15—C16—H16   | 120.2     |
| C2—C3—C11  | 111.3 (2) | C17—C16—H16   | 120.2     |
| C5—C4—C9   | 119.0 (3) | C16—C17—C18   | 121.9 (3) |
| C5—C4—C3   | 131.1 (3) | C16—C17—H17   | 119.0     |
| C9—C4—C3   | 109.9 (2) | C18—C17—H17   | 119.0     |
| C4—C5—C6   | 119.0 (3) | C17—C18—C13   | 118.3 (3) |
| C4—C5—H5   | 120.5     | C17—C18—C19   | 118.9 (3) |
| C6—C5—H5   | 120.5     | C13—C18—C19   | 122.8 (2) |
| C7—C6—C5   | 120.5 (3) | C24—C19—C20   | 117.8 (3) |



|               |            |                 |            |
|---------------|------------|-----------------|------------|
| C7—C6—H6      | 119.7      | C24—C19—C18     | 123.3 (2)  |
| C5—C6—H6      | 119.7      | C20—C19—C18     | 118.8 (3)  |
| C6—C7—C8      | 121.6 (3)  | C21—C20—C19     | 120.9 (3)  |
| C6—C7—H7      | 119.2      | C21—C20—H20     | 119.5      |
| C8—C7—H7      | 119.2      | C19—C20—H20     | 119.5      |
| C9—C8—C7      | 116.6 (3)  | C22—C21—C20     | 120.8 (3)  |
| C9—C8—H8      | 121.7      | C22—C21—H21     | 119.6      |
| C7—C8—H8      | 121.7      | C20—C21—H21     | 119.6      |
| C8—C9—C4      | 123.3 (3)  | C21—C22—C23     | 119.2 (3)  |
| C8—C9—N1      | 127.9 (3)  | C21—C22—H22     | 120.4      |
| C4—C9—N1      | 108.8 (2)  | C23—C22—H22     | 120.4      |
| C3—C10—H10A   | 109.5      | C24—C23—C22     | 120.4 (3)  |
| C3—C10—H10B   | 109.5      | C24—C23—H23     | 119.8      |
| H10A—C10—H10B | 109.5      | C22—C23—H23     | 119.8      |
| C3—C10—H10C   | 109.5      | C23—C24—C19     | 120.9 (3)  |
| H10A—C10—H10C | 109.5      | C23—C24—H24     | 119.6      |
| H10B—C10—H10C | 109.5      | C19—C24—H24     | 119.6      |
| C3—C11—H11A   | 109.5      |                 |            |
| C12—N2—N3—C13 | 173.1 (2)  | C2—N1—C9—C4     | 2.7 (3)    |
| C9—N1—C2—C12  | 175.1 (2)  | C1—N1—C9—C4     | -174.8 (2) |
| C1—N1—C2—C12  | -7.4 (4)   | N1—C2—C12—N2    | 176.2 (2)  |
| C9—N1—C2—C3   | -3.1 (3)   | C3—C2—C12—N2    | -6.1 (4)   |
| C1—N1—C2—C3   | 174.4 (2)  | N3—N2—C12—C2    | 177.9 (2)  |
| C12—C2—C3—C4  | -175.8 (3) | N2—N3—C13—C14   | -10.7 (4)  |
| N1—C2—C3—C4   | 2.2 (3)    | N2—N3—C13—C18   | 172.1 (2)  |
| C12—C2—C3—C10 | -57.5 (4)  | N3—C13—C14—C15  | -173.7 (3) |
| N1—C2—C3—C10  | 120.6 (3)  | C18—C13—C14—C15 | 3.5 (4)    |
| C12—C2—C3—C11 | 65.5 (3)   | C13—C14—C15—C16 | 0.5 (4)    |
| N1—C2—C3—C11  | -116.5 (2) | C14—C15—C16—C17 | -3.5 (4)   |
| C10—C3—C4—C5  | 60.5 (4)   | C15—C16—C17—C18 | 2.5 (4)    |
| C2—C3—C4—C5   | 179.0 (3)  | C16—C17—C18—C13 | 1.5 (4)    |
| C11—C3—C4—C5  | -62.7 (4)  | C16—C17—C18—C19 | -177.2 (2) |
| C10—C3—C4—C9  | -119.1 (2) | C14—C13—C18—C17 | -4.4 (4)   |
| C2—C3—C4—C9   | -0.6 (3)   | N3—C13—C18—C17  | 172.9 (2)  |
| C11—C3—C4—C9  | 117.7 (3)  | C14—C13—C18—C19 | 174.2 (3)  |
| C9—C4—C5—C6   | 0.5 (4)    | N3—C13—C18—C19  | -8.5 (4)   |
| C3—C4—C5—C6   | -179.0 (3) | C17—C18—C19—C24 | -132.0 (3) |
| C4—C5—C6—C7   | -0.2 (5)   | C13—C18—C19—C24 | 49.4 (4)   |
| C5—C6—C7—C8   | -0.2 (5)   | C17—C18—C19—C20 | 45.8 (4)   |
| C6—C7—C8—C9   | 0.3 (4)    | C13—C18—C19—C20 | -132.8 (3) |
| C7—C8—C9—C4   | 0.1 (4)    | C24—C19—C20—C21 | 0.4 (4)    |
| C7—C8—C9—N1   | -179.6 (3) | C18—C19—C20—C21 | -177.5 (3) |
| C5—C4—C9—C8   | -0.5 (4)   | C19—C20—C21—C22 | -0.2 (4)   |
| C3—C4—C9—C8   | 179.2 (2)  | C20—C21—C22—C23 | -0.3 (5)   |
| C5—C4—C9—N1   | 179.3 (2)  | C21—C22—C23—C24 | 0.7 (5)    |
| C3—C4—C9—N1   | -1.1 (3)   | C22—C23—C24—C19 | -0.6 (5)   |
| C2—N1—C9—C8   | -177.6 (3) | C20—C19—C24—C23 | 0.0 (4)    |
| C1—N1—C9—C8   | 4.9 (4)    | C18—C19—C24—C23 | 177.8 (3)  |

## Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

Cg1, Cg2 and Cg3 are the centroids of the C19–C24, C4–C9 and C13–C18 rings, respectively.

| $D-H\cdots A$                        | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C1—H1C $\cdots$ Cg1 <sup>i</sup>     | 0.98  | 2.86        | 3.582 (3)   | 131           |
| C1—H1A $\cdots$ Cg1 <sup>ii</sup>    | 0.98  | 3.02        | 3.948 (3)   | 160           |
| C11—H11B $\cdots$ Cg3 <sup>iii</sup> | 0.98  | 2.74        | 3.721 (3)   | 179           |
| C22—H22 $\cdots$ Cg2 <sup>iv</sup>   | 0.95  | 2.76        | 3.645 (3)   | 155           |

Symmetry codes: (i)  $x+1/2, -y+2, z$ ; (ii)  $x, y+1, z$ ; (iii)  $x+1/2, -y+1, z$ ; (iv)  $-x+1, -y+2, z-1/2$ .

Fig. 1

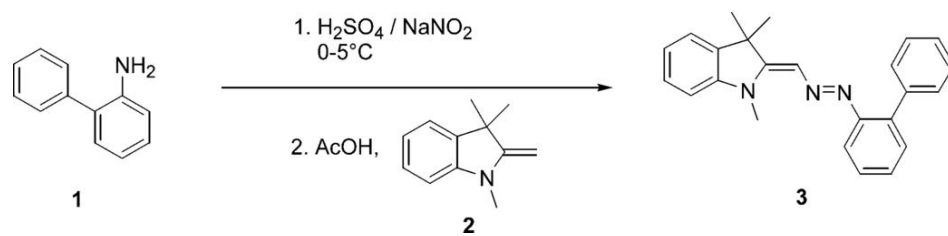


Fig. 2

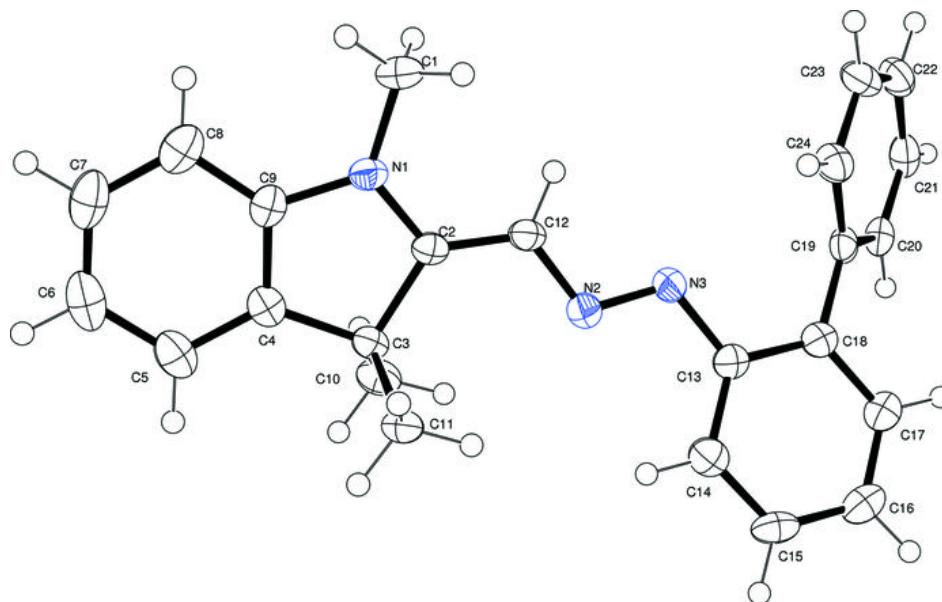


Fig. 3

