Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,2′-(Propane-1,3-diyl)bis(2*H*-indazole)

Saúl Ovalle,[a] Sylvain Bernès,[b] Nancy Pérez Rodríguez[a] and Perla Elizondo Martínez[a]*

[a]Laboratorio de Química Industrial, Centro de Laboratorios Especializados, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Pedro de Alba S/N, 66451 San Nicolás de los Garza, NL, Mexico, and [b]División de Estudios de Posgrado, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Guerrero y Progreso S/N, Col. Treviño, 64570 Monterrey, NL, Mexico
Correspondence e-mail: sylvain_bernes@hotmail.com

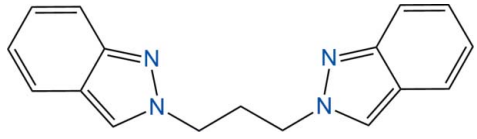
Received 14 June 2011; accepted 18 July 2011

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.049; wR factor = 0.162; data-to-parameter ratio = 13.7.

The title molecule, $C_{17}H_{16}N_4$, is a bis-indazole crystallized in the rare 2*H*-tautomeric form. Indazole heterocycles are connected by a propane C_3 chain, and the molecule is placed on a general position, in contrast to the analogous compound with a central C_2 ethane bridge, which was previously found to be placed on an inversion center in the same space group. In the title molecule, indazole rings make a dihedral angle of 60.11 (7)°, and the bridging alkyl chain displays a *trans* conformation, resulting in a W-shaped molecule. In the crystal, molecules interact weakly through π–π contacts between inversion-related pyrazole rings, with a centroid–centroid separation of 3.746 (2) Å.

Related literature

For the synthesis of 2*H*-indazoles, see: Wu *et al.* (2010). For studies of 1*H*←→2*H* tautomerism in indazoles, see: Alkorta & Elguero (2005); Yu *et al.* (2006). For 2*H*-indazole X-ray structures, see: Saczewski *et al.* (2001); Rodríguez de Barbarín *et al.* (2006); Ramos Silva *et al.* (2008); Hurtado *et al.* (2009); Zhou *et al.* (2010); Long *et al.* (2011).



Experimental

Crystal data

$C_{17}H_{16}N_4$
M_r = 276.34
Orthorhombic, *Pbca*
a = 8.182 (2) Å
b = 10.549 (4) Å
c = 34.179 (9) Å
V = 2950.1 (16) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 298 K
0.60 × 0.40 × 0.18 mm

Data collection

Siemens P4 diffractometer
8195 measured reflections
2621 independent reflections
1607 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
3 standard reflections every 97 reflections
intensity decay: 1.5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.162
S = 1.10
2621 reflections
191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

The authors thank the PAICyT program (Programa de Apoyo a la Investigación Científica y Tecnológica) of the Universidad Autónoma de Nuevo León for supporting this work (project No. T004–09).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AA2015).

References

Alkorta, I. & Elguero, J. (2005). *J. Phys. Org. Chem.* **18**, 719–724.
Hurtado, J., Mac-Leod Carey, D., Muñoz-Castro, A., Arratia-Pérez, R., Quijada, R., Wu, G., Rojas, R. & Valderrama, M. (2009). *J. Organomet. Chem.* **694**, 2636–2641.
Long, L., Liu, B.-N., Liu, M. & Liu, D.-K. (2011). *Acta Cryst.* E**67**, o1546.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Ramos Silva, M., Moreira, V. M., Cardoso, C., Matos Beja, A. & Salvador, J. A. R. (2008). *Acta Cryst.* C**64**, o217–o219.
Rodríguez de Barbarín, C., Nájera, B., Elizondo, P. & Cerda, P. (2006). *Acta Cryst.* E**62**, o5423–o5424.
Saczewski, F., Saczewski, J. & Gdaniec, M. (2001). *Chem. Pharm. Bull.* **49**, 1203–1206.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1996). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Wu, C., Fang, Y., Larock, R. C. & Shi, F. (2010). *Org. Lett.* **12**, 2234–2237.
Yu, H.-Y., Li, B.-Z. & Guo, Y.-M. (2006). *Chin. J. Chem. Phys.* **19**, 233–237.
Zhou, X., Qin, X. & Zhang, J. (2010). *Acta Cryst.* E**66**, o2732.

supplementary materials

Acta Cryst. (2011). E**67**, o2144 [**doi:10.1107/S1600536811029011**]

2,2'-(Propane-1,3-diyl)bis(2*H*-indazole)

S. Ovalle, S. Bernès, N. Pérez Rodríguez and P. Elizondo Martínez

Comment

Although efficient synthetic routes for 2*H*-indazoles are available (*e.g.* Wu *et al.*, 2010) few molecules belonging to this family of heterocyclic compounds have been X-ray characterized up to now. This is due, in part, to the fact that 1*H* tautomer for indazoles is frequently more stable than the 2*H* tautomer, although the opposite situation may occur for some derivatives (Alkorta & Elguero, 2005; Yu *et al.*, 2006). On the other hand, in the case of N2-substituted indazoles, only the 2*H* tautomer is allowed. Tautomerism equilibrium study is important, since bioavailability and other pharmacological properties of indazoles may be dependent on such equilibria (*e.g.* Ramos Silva *et al.*, 2008). Indazole derivatives have been used, for instance, for their anti-inflammatory activity.

The title compound was prepared through a three steps procedure, the key step being the cyclization of a nitroamine derivative (compound **P**, see Fig. 1 and *Experimental*). The resulting bis-indazole consists of two 2*H*-indazole heterocycles connected by an alkyl C_3 bridge (Fig. 2). The molecule lies in a general position, in space group *Pbca*. It is worth noting that the analogue compound with a central C_2 bridge, for which we reported the X-ray structure (Rodríguez de Barbarín *et al.*, 2006), was found to crystallize in the same space group, although the molecule was placed on an inversion center. From this pair of structures now determined, we can propose the following general rule for *n*-alkyl bridged bis(2*H*-indazoles): even-alkyl compounds should be centrosymmetric, while odd-alkyl derivatives are expected to be non-centrosymmetric, as the title compound.

Molecular dimensions observed in the title compound compare well with those reported for other 2*H*-indazoles (Saczewski *et al.*, 2001; Rodríguez de Barbarín *et al.*, 2006; Hurtado *et al.*, 2009; Zhou *et al.*, 2010; Long *et al.*, 2011). Indazole rings make a dihedral angle of 60.11 (7)°. Torsion angles N2—C8—C9—C10 and C8—C9—C10—N12, -176.7 (2) and 173.5 (2)° respectively, characterize the *trans* conformation for the alkyl bridge, resulting in a W-shaped molecule. The crystal structure features π–π interactions of modest strength, between molecules related by inversion (Fig. 3). The separation between the centroid of the pyrazole ring N11/N12/C11/C17/C16 and the symmetry-related centroid at position -*x*, 1 - *y*, 1 - *z*, is 3.746 (2) Å.

Experimental

The title ligand, **PI**, was obtained by a three steps reaction procedure (Fig. 1). The condensation between 1,3-diaminopropane and 2-nitrobenzaldehyde produced the corresponding imine. Selective reduction of imine bonds with sodium borohydride in methanol gave amine **P**, which was isolated. Then, 0.044 g of Pd/C was added to a solution of **P** (0.005 mol) in ethanol. This mixture was refluxed for 5.5 h, with addition of hydrazine monohydrate (0.110 mol) during the first 3 h. The mixture was filtered, distilled, and the organic phase was extracted. The product was purified by column chromatography with silica gel and ethyl acetate:hexane (2:1) as eluent. Suitable crystals were obtained by slow evaporation of an ethanol solution at 298 K. Mp 389.4–390 K; analysis found (calc. for $C_{17}H_{16}N_4$): C 73.6 (73.9), H 5.8 (5.8), N 20.5% (20.3%); IR RTA: 3108 (CH Ar. ν_s), 2950 (–CH_2– ν_s), 1625 (C=N Ar. δ_s), 1514, 1467 (C=C Ar. ν_s and ν_{as}). ^{1}H NMR (300 MHz, $CDCl_3$):

δ, p.p.m.: 2.73 (2*H*, m, –CH_2–), 4.41 (4*H*, t, N—CH_2), 7.10 (2*H*, dd, Ar), 7.31 (2*H*, dd, Ar), 7.66 (2*H*, dd, Ar), 7.73 (2*H*, td, Ar), 7.95 (2*H*, s, NH).

Refinement

All H atoms were placed in idealized positions and refined as riding to their parent C atoms, with bond lengths fixed to 0.97 (methylene CH_2) or 0.93 Å (aromatic CH). Isotropic displacement parameters for H atoms were calculated as U_{iso}(H) = 1.2 U_{eq}(carrier atom).

Figures

Fig. 1. Synthetic route for the title compound. **P** is the key intermediate and **PI** is the title compound.

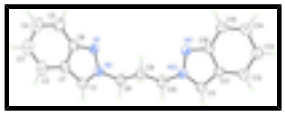


Fig. 2. *ORTEP*-like view of the title molecule, with displacement ellipsoids at the 30% probability level for non-H atoms.

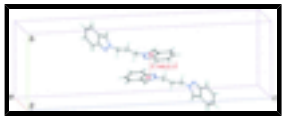


Fig. 3. A part of the crystal structure representing two molecules related by inversion, which interact through a π–π contact involving pyrazole rings (dashed line).

2,2'-(Propane-1,3-diyl)bis(2*H*-indazole)

Crystal data

$C_{17}H_{16}N_4$	D_x = 1.244 Mg m^{-3}
M_r = 276.34	Melting point: 389 K
Orthorhombic, *Pbca*	Mo *K*α radiation, λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 77 reflections
a = 8.182 (2) Å	θ = 4.6–12.4°
b = 10.549 (4) Å	μ = 0.08 mm^{-1}
c = 34.179 (9) Å	*T* = 298 K
V = 2950.1 (16) Å^3	Prism, yellow
Z = 8	0.60 × 0.40 × 0.18 mm
F(000) = 1168	

Data collection

Siemens P4 diffractometer	R_{int} = 0.042
Radiation source: fine-focus sealed tube	θ_{max} = 25.1°, θ_{min} = 2.4°
graphite	*h* = −9→8
ω scans	*k* = −12→12
8195 measured reflections	*l* = −40→40
2621 independent reflections	3 standard reflections every 97 reflections

1607 reflections with $I > 2\sigma(I)$

intensity decay: 1.5%

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.162$

$S = 1.10$

2621 reflections

191 parameters

0 restraints

0 constraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.9616P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.20$ e Å^{-3}

$\Delta\rho_{min} = -0.21$ e Å^{-3}

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0159 (17)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.3628 (3)	0.67210 (17)	0.33910 (5)	0.0640 (6)
N2	0.2422 (2)	0.75293 (17)	0.34924 (5)	0.0563 (5)
C1	0.2608 (3)	0.8690 (2)	0.33476 (6)	0.0622 (7)
H1A	0.1914	0.9378	0.3385	0.075*
C2	0.4896 (4)	0.9559 (3)	0.29004 (7)	0.0773 (8)
H2A	0.4529	1.0390	0.2876	0.093*
C3	0.6261 (5)	0.9172 (3)	0.27178 (8)	0.0902 (10)
H3A	0.6828	0.9744	0.2561	0.108*
C4	0.6856 (4)	0.7935 (4)	0.27562 (9)	0.0986 (11)
H4A	0.7815	0.7708	0.2628	0.118*
C5	0.6062 (4)	0.7056 (3)	0.29769 (8)	0.0847 (9)
H5A	0.6463	0.6235	0.3002	0.102*
C6	0.4614 (3)	0.7431 (2)	0.31655 (6)	0.0610 (7)
C7	0.4032 (3)	0.8675 (2)	0.31308 (6)	0.0604 (7)
C8	0.1158 (3)	0.7097 (2)	0.37586 (6)	0.0639 (7)
H8A	0.0822	0.6247	0.3686	0.077*
H8B	0.0214	0.7649	0.3737	0.077*
C9	0.1757 (3)	0.7094 (2)	0.41760 (7)	0.0646 (7)
H9A	0.2737	0.6582	0.4195	0.078*
H9B	0.2031	0.7952	0.4254	0.078*
C10	0.0474 (3)	0.6575 (3)	0.44453 (6)	0.0671 (7)
H10B	−0.0458	0.7143	0.4447	0.080*
H10C	0.0109	0.5760	0.4348	0.080*
N11	0.2399 (2)	0.56892 (18)	0.49101 (5)	0.0611 (6)
N12	0.1075 (2)	0.64232 (18)	0.48438 (5)	0.0571 (5)
C11	0.0399 (3)	0.6887 (2)	0.51674 (7)	0.0615 (7)

H11B	−0.0516	0.7409	0.5181	0.074*
C12	0.1239 (4)	0.6545 (2)	0.58912 (7)	0.0696 (7)
H12B	0.0444	0.7040	0.6012	0.083*
C13	0.2351 (3)	0.5902 (3)	0.61062 (7)	0.0699 (7)
H13B	0.2306	0.5947	0.6378	0.084*
C14	0.3567 (3)	0.5170 (2)	0.59287 (8)	0.0707 (7)
H14C	0.4308	0.4737	0.6086	0.085*
C15	0.3702 (3)	0.5070 (2)	0.55328 (7)	0.0683 (7)
H15B	0.4538	0.4603	0.5418	0.082*
C16	0.2530 (3)	0.5701 (2)	0.53037 (6)	0.0533 (6)
C17	0.1312 (3)	0.6448 (2)	0.54797 (7)	0.0555 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0772 (15)	0.0555 (11)	0.0593 (11)	0.0036 (11)	0.0102 (11)	0.0011 (9)
N2	0.0647 (13)	0.0543 (10)	0.0499 (10)	0.0009 (10)	0.0040 (10)	0.0007 (8)
C1	0.0780 (18)	0.0525 (13)	0.0560 (13)	0.0050 (12)	−0.0062 (14)	0.0031 (10)
C2	0.107 (2)	0.0695 (16)	0.0558 (14)	−0.0202 (17)	−0.0037 (16)	0.0056 (12)
C3	0.113 (3)	0.095 (2)	0.0633 (17)	−0.036 (2)	0.0138 (18)	0.0004 (15)
C4	0.100 (3)	0.118 (3)	0.0780 (19)	−0.011 (2)	0.0320 (18)	−0.0046 (19)
C5	0.095 (2)	0.0832 (19)	0.0754 (17)	0.0069 (18)	0.0252 (17)	−0.0047 (15)
C6	0.0760 (17)	0.0596 (14)	0.0474 (12)	−0.0041 (13)	0.0039 (12)	−0.0038 (10)
C7	0.0796 (18)	0.0570 (13)	0.0447 (12)	−0.0064 (13)	−0.0031 (12)	0.0003 (10)
C8	0.0633 (16)	0.0713 (15)	0.0572 (13)	−0.0018 (13)	0.0053 (12)	0.0041 (11)
C9	0.0662 (17)	0.0707 (15)	0.0570 (13)	−0.0090 (13)	0.0045 (12)	0.0051 (12)
C10	0.0665 (17)	0.0764 (16)	0.0583 (14)	−0.0086 (14)	0.0020 (13)	0.0044 (12)
N11	0.0601 (13)	0.0607 (12)	0.0626 (11)	0.0070 (10)	0.0088 (10)	0.0013 (9)
N12	0.0542 (12)	0.0595 (11)	0.0576 (11)	0.0007 (10)	0.0071 (10)	0.0047 (9)
C11	0.0608 (16)	0.0610 (14)	0.0628 (15)	0.0081 (12)	0.0103 (12)	0.0004 (11)
C12	0.0737 (18)	0.0719 (16)	0.0631 (15)	0.0076 (15)	0.0085 (14)	−0.0050 (12)
C13	0.0792 (19)	0.0731 (16)	0.0574 (13)	0.0005 (16)	−0.0023 (14)	0.0011 (12)
C14	0.0732 (19)	0.0667 (15)	0.0724 (16)	0.0059 (14)	−0.0063 (14)	0.0087 (13)
C15	0.0687 (17)	0.0639 (14)	0.0724 (16)	0.0098 (13)	0.0054 (14)	0.0012 (12)
C16	0.0535 (14)	0.0470 (11)	0.0593 (13)	−0.0014 (11)	0.0061 (11)	0.0023 (10)
C17	0.0570 (15)	0.0505 (12)	0.0590 (13)	0.0018 (11)	0.0072 (12)	0.0015 (10)

Geometric parameters (Å, °)

N1—C6	1.343 (3)	C9—H9A	0.9700
N1—N2	1.350 (3)	C9—H9B	0.9700
N2—C1	1.329 (3)	C10—N12	1.457 (3)
N2—C8	1.451 (3)	C10—H10B	0.9700
C1—C7	1.381 (4)	C10—H10C	0.9700
C1—H1A	0.9300	N11—C16	1.350 (3)
C2—C3	1.343 (4)	N11—N12	1.351 (3)
C2—C7	1.410 (3)	N12—C11	1.330 (3)
C2—H2A	0.9300	C11—C17	1.383 (3)
C3—C4	1.400 (5)	C11—H11B	0.9300

C3—H3A	0.9300	C12—C13	1.353 (4)
C4—C5	1.360 (4)	C12—C17	1.411 (3)
C4—H4A	0.9300	C12—H12B	0.9300
C5—C6	1.406 (4)	C13—C14	1.398 (4)
C5—H5A	0.9300	C13—H13B	0.9300
C6—C7	1.401 (3)	C14—C15	1.362 (4)
C8—C9	1.509 (3)	C14—H14C	0.9300
C8—H8A	0.9700	C15—C16	1.405 (3)
C8—H8B	0.9700	C15—H15B	0.9300
C9—C10	1.499 (3)	C16—C17	1.406 (3)
C6—N1—N2	103.55 (18)	C10—C9—H9B	109.5
C1—N2—N1	113.7 (2)	C8—C9—H9B	109.5
C1—N2—C8	127.2 (2)	H9A—C9—H9B	108.1
N1—N2—C8	118.95 (18)	N12—C10—C9	112.2 (2)
N2—C1—C7	106.6 (2)	N12—C10—H10B	109.2
N2—C1—H1A	126.7	C9—C10—H10B	109.2
C7—C1—H1A	126.7	N12—C10—H10C	109.2
C3—C2—C7	118.4 (3)	C9—C10—H10C	109.2
C3—C2—H2A	120.8	H10B—C10—H10C	107.9
C7—C2—H2A	120.8	C16—N11—N12	103.05 (18)
C2—C3—C4	121.9 (3)	C11—N12—N11	113.89 (19)
C2—C3—H3A	119.0	C11—N12—C10	126.6 (2)
C4—C3—H3A	119.0	N11—N12—C10	119.37 (19)
C5—C4—C3	121.5 (3)	N12—C11—C17	107.1 (2)
C5—C4—H4A	119.3	N12—C11—H11B	126.5
C3—C4—H4A	119.3	C17—C11—H11B	126.5
C4—C5—C6	117.7 (3)	C13—C12—C17	118.5 (2)
C4—C5—H5A	121.1	C13—C12—H12B	120.8
C6—C5—H5A	121.1	C17—C12—H12B	120.8
N1—C6—C7	111.5 (2)	C12—C13—C14	121.4 (2)
N1—C6—C5	127.7 (2)	C12—C13—H13B	119.3
C7—C6—C5	120.7 (2)	C14—C13—H13B	119.3
C1—C7—C6	104.6 (2)	C15—C14—C13	122.1 (2)
C1—C7—C2	135.6 (3)	C15—C14—H14C	118.9
C6—C7—C2	119.8 (3)	C13—C14—H14C	118.9
N2—C8—C9	111.3 (2)	C14—C15—C16	117.5 (2)
N2—C8—H8A	109.4	C14—C15—H15B	121.2
C9—C8—H8A	109.4	C16—C15—H15B	121.2
N2—C8—H8B	109.4	N11—C16—C15	127.3 (2)
C9—C8—H8B	109.4	N11—C16—C17	112.0 (2)
H8A—C8—H8B	108.0	C15—C16—C17	120.7 (2)
C10—C9—C8	110.7 (2)	C11—C17—C16	103.9 (2)
C10—C9—H9A	109.5	C11—C17—C12	136.2 (2)
C8—C9—H9A	109.5	C16—C17—C12	119.8 (2)
C6—N1—N2—C1	−0.6 (2)	C8—C9—C10—N12	173.5 (2)
C6—N1—N2—C8	−176.64 (19)	C16—N11—N12—C11	0.5 (3)
N1—N2—C1—C7	0.3 (3)	C16—N11—N12—C10	−176.1 (2)
C8—N2—C1—C7	176.0 (2)	C9—C10—N12—C11	126.4 (3)

C7—C2—C3—C4	−1.2 (4)	C9—C10—N12—N11	−57.4 (3)
C2—C3—C4—C5	1.0 (5)	N11—N12—C11—C17	0.0 (3)
C3—C4—C5—C6	0.2 (5)	C10—N12—C11—C17	176.3 (2)
N2—N1—C6—C7	0.6 (3)	C17—C12—C13—C14	1.0 (4)
N2—N1—C6—C5	−179.3 (2)	C12—C13—C14—C15	0.3 (4)
C4—C5—C6—N1	178.9 (3)	C13—C14—C15—C16	−2.1 (4)
C4—C5—C6—C7	−1.0 (4)	N12—N11—C16—C15	179.2 (2)
N2—C1—C7—C6	0.1 (2)	N12—N11—C16—C17	−0.8 (2)
N2—C1—C7—C2	178.5 (3)	C14—C15—C16—N11	−177.3 (2)
N1—C6—C7—C1	−0.5 (3)	C14—C15—C16—C17	2.7 (4)
C5—C6—C7—C1	179.5 (2)	N12—C11—C17—C16	−0.5 (3)
N1—C6—C7—C2	−179.2 (2)	N12—C11—C17—C12	−177.6 (3)
C5—C6—C7—C2	0.8 (4)	N11—C16—C17—C11	0.8 (3)
C3—C2—C7—C1	−177.9 (3)	C15—C16—C17—C11	−179.2 (2)
C3—C2—C7—C6	0.4 (4)	N11—C16—C17—C12	178.5 (2)
C1—N2—C8—C9	−97.6 (3)	C15—C16—C17—C12	−1.5 (3)
N1—N2—C8—C9	77.9 (3)	C13—C12—C17—C11	176.4 (3)
N2—C8—C9—C10	−176.7 (2)	C13—C12—C17—C16	−0.4 (4)

Fig. 1

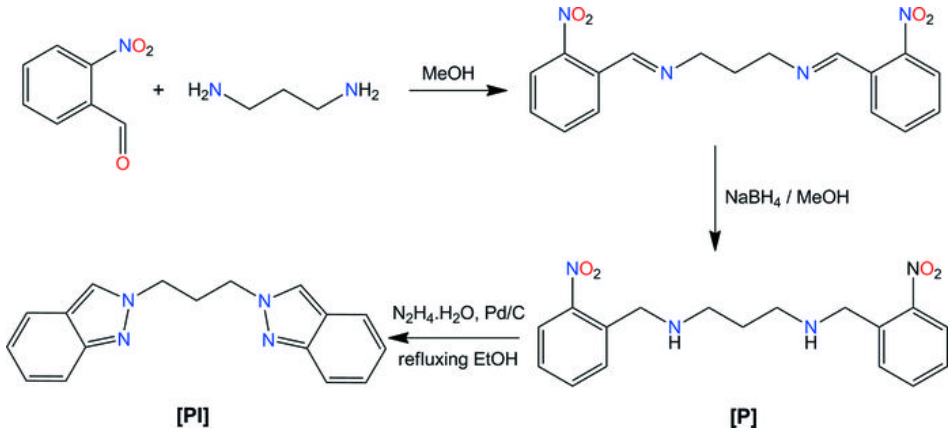

NO2
+
H2N
NH2
MeOH
NO2
NO2
N
N
NaBH4 / MeOH
NO2
NO2
N
H
N
H
N2H4.H2O, Pd/C
refluxing EtOH
N
N
N
N
[PI]
[P]

Fig. 2

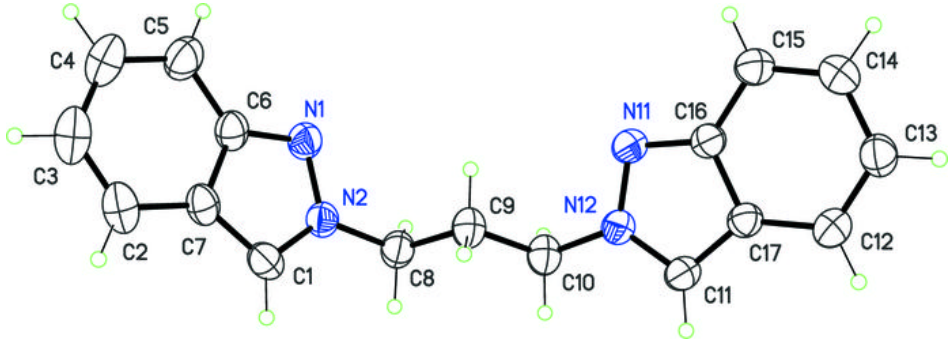

C5
C4
C6
N1
C3
N2
C9
N12
N11
C16
C15
C14
C13
C2
C7
C1
C8
C10
C11
C17
C12

Fig. 3