5,12-Dimethyl-3,10-diphenyl-1,3,4,8,10,11-hexaazatetra-cyclo[6.6.1.0^{2,6}.0^{9,13}]pentadeca-2(6),4,9(13),11-tetraene, a new Tröger's base analogue

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The synthesis of the title Tröger's base analogue, $C_{23}H_{22}N_6$, was undertaken in order to study the influence of a methyl substituent on the structure. Minor differences were found in the bond lengths of the title structure in comparison with the values for free pyrazole and for the first pyrazolic Tröger's base reported in the literature. There are two molecules of opposite chirality in the asymmetric unit and the packing in the lattice is characterized by a non-crystallographic n-glide plane relating these molecules.

Comment

As part of an ongoing study of the reactivity of pyrazole derivatives as activated aromatic precursors (Quiroga *et al.*, 1999), the synthesis of fused amino-heterocyclic systems was undertaken to obtain a compound with a five-membered aromatic ring, *i.e.* a new Tröger's base. The molecular structure of 3,4;7,8-bis(1-phenylpyrazolo)-1,5-methylene-1,5-diazacy-clooctane {alternatively 3,10-diphenyl-1,3,4,8,10,11-hexaaza-tetracyclo[6.6.1.0^{2,6}.0^{9,13}]pentadeca-2(6),4,9(13),11-tetraene}, the first pyrazolic Tröger's base, has been reported in the literature (Cudero *et al.*, 1997). In the Cambridge Structural Database (Allen *et al.*, 1991), this compound has the refcode NIMHIA. Tröger's bases are concave chiral molecules with interesting structural properties. Several Tröger's base analogues with potential applications in the design of synthetic enzymes, artificial receptor systems, selective organic catalysts and reagents (Cowart *et al.*, 1988; Adrian & Wilcox, 1992), chelating and biomimetic systems (Wilcox, 1985; Crossley *et*

al., 1995) and metal complexes with catalytic activity (Gold-berg & Alper, 1995) have been reported. The title Tröger's base, (II), was synthesized from 5-amino-3-methyl-1-phenyl-pyrazole, (I), by reaction with formaldehyde.
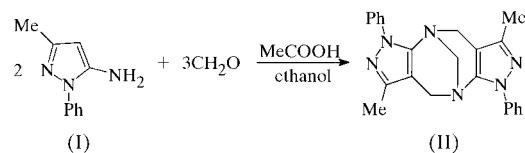
Compound (II) (Fig. 1) has a folded structure wherein the two N atoms and the three methylene C atoms form a hinge-like bridge between the two pyrazole rings. Comparing the bond lengths of free pyrazole (Larsen *et al.*, 1970) with the pyrazole moiety in the title compound, it was found that the N—N bond lengths change from 1.334 and 1.338 Å in the free
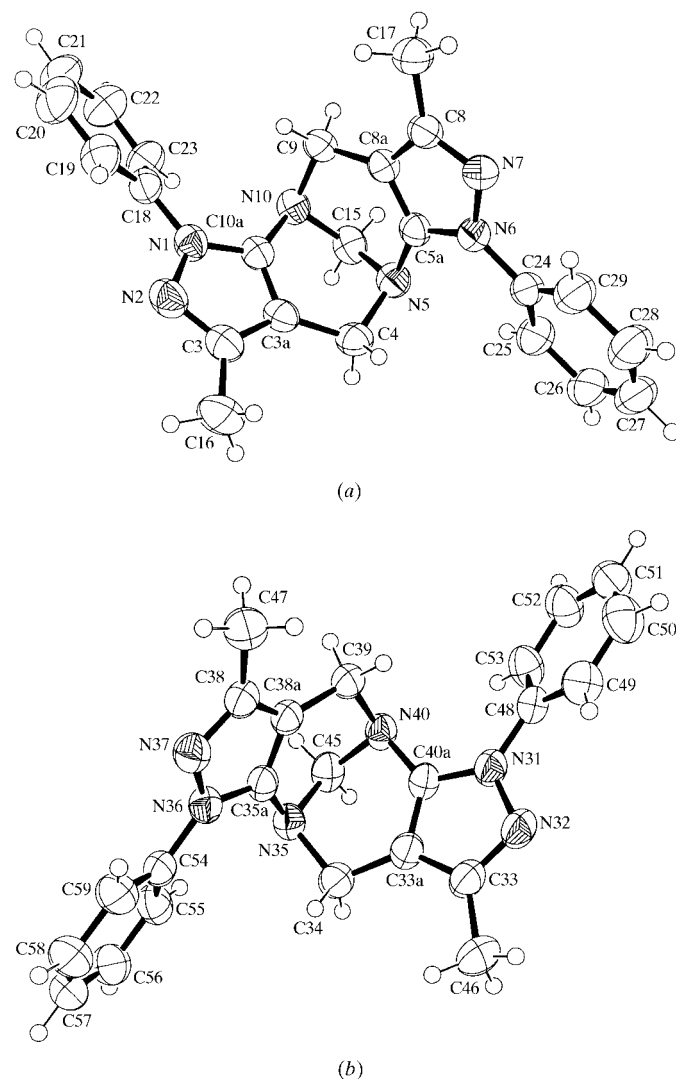
Figure 1
An *ORTEP*-3 (Farrugia, 1997) plot of the two molecules of the title compound with the atomic labelling scheme. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The atom labels indicate the presence of the pseudo-n-glide plane.

organic compounds

molecule to 1.374 (2) Å for N1—N2, 1.380 (2) Å for N6—N7, 1.375 (2) Å for N31—N32 and 1.377 (2) Å for N36—N37 in the title compound. The C—N bond lengths in free pyrazole change from 1.325 and 1.339 Å to 1.358 (3) Å for N1—C10a, 1.371 (3) Å for N6—C5a, 1.359 (2) Å for N31—C40a and 1.371 (2) Å for N36—C35a in (II). The values of the bond angles of the pyrazole ring of the free molecule and of the pyrazole moiety of (II) are similar. When the bond lengths and angles of the eight-membered ring in NIMHIA are compared with the bond lengths and angles of the same ring in (II), minor differences are found. The other bond-length values of the phenyl and pyrazole rings of the NIMHIA structure are very close to those in the title structure. The tetrahydro-pyrimidine backbone adopts a half-chair conformation (Cremer & Pople, 1975). This conformation is similar to that in NIMHIA. In Tröger's bases, the dihedral angle formed by the least-squares planes containing the aryl substituent rings varies from 92 to 104° (Wilcox *et al.*, 1987). This same dihedral angle in NIMHIA has a value of 96.4 (4)°, while in compound (II), the values are 85.95 (7) and 86.82 (9)°. There are two molecules of opposite chirality in the asymmetric unit and the packing in the lattice is characterized by a non-crystallographic *n*-glide plane relating these molecules. These mol-
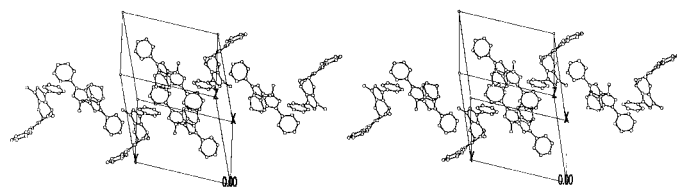
Figure 2
A *ZORTEP* (Zsolnai, 1995) stereoscopic packing view of the title compound showing the two independent enantiomers related by a non-crystallographic *n*-glide plane.

ecules also exhibit *dyad* symmetry. The equation found for the glide plane is $0.0178x + 0.0006y + 0.9998z - 5.1954 = 0$ and the translations are approximately $(a + b)/2$. Fig. 2 shows the packing of the two independent enantiomers related by the pseudo-*n*-glide plane.

Experimental

5-Amino-3-methyl-1-phenylpyrazole, (I) (2.89 mmol), formaldehyde 37% (4.5 mmol) and acetic acid (0.2 ml) in ethanol (10 ml) were heated at 323 K for 5 min and monitored by thin-layer chromatography. After cooling, crystals were obtained, filtered off and recrystallized from ethanol [yield 53%; m.p. 551 (1) K]. ^{1}H NMR (300 MHz, DMSO-d_6): δ (p.p.m.) 1.92 (6H, *s*), 3.56 (2H, *d*, *J* = 15.7 Hz), 4.26 (2H, *d*, *J* = 15.7 Hz), 4.31 (2H, *s*), 7.29 (2H, *t*, *J* = 7.4 Hz), 7.50 (4H, br *t*, *J* = 7.9 Hz), 7.96 (4H, *d*, *J* = 8.7 Hz); ^{13}C NMR (75 MHz, DMSO-d_6): δ (p.p.m.) 12.1 (C-16, C-17), 47.4 (C-4, C-9), 67.5 (C-15), 104.3, 119.7, 125.5, 129.3, 139.2, 144.7, 144.9; MS (70 eV): *m/e* (%) 382 (100), 354 (23), 198 (53), 77 (30); $C_{23}H_{22}N_6$ (382.46), calculated: C 72.19, H 5.81, N 22.01%; found: C 72.13, H 5.82, N 22.05%.

Crystal data

$C_{23}H_{22}N_6$	$Z = 4$
$M_r = 382.46$	$D_x = 1.290$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 11.1240\ (10)$ Å	Cell parameters from 17
$b = 13.6500\ (10)$ Å	reflections
$c = 14.1100\ (10)$ Å	$\theta = 20.52$–$22.45°$
$\alpha = 75.270\ (2)°$	$\mu = 0.080$ mm^{-1}
$\beta = 73.070\ (2)°$	$T = 293$ K
$\gamma = 76.270\ (2)°$	Transparent prism, colourless
$V = 1968.7\ (3)$ Å^3	$0.20 \times 0.15 \times 0.12$ mm

Data collection

Rigaku AFC-7*S* diffractometer	$h = -13 \rightarrow 13$
$\omega/2\theta$ scans	$k = -16 \rightarrow 0$
7664 measured reflections	$l = -17 \rightarrow 16$
7332 independent reflections	3 standard reflections
4249 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.091$	intensity decay: 3.6%
$\theta_{max} = 25.49°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0738P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.043$	$+ 0.0251P]$
$wR(F^2) = 0.141$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.016$	$(\Delta/\sigma)_{max} < 0.001$
7332 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
570 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
H atoms constrained	

Table 1
Selected geometric parameters (Å, °).

C4—N5	1.490 (3)	C34—N35	1.487 (3)
N5—C5a	1.409 (2)	N35—C35a	1.408 (3)
N5—C15	1.472 (3)	N35—C45	1.477 (3)
C9—N10	1.489 (2)	C39—N40	1.484 (3)
N10—C10a	1.412 (2)	N40—C40a	1.410 (2)
N10—C15	1.474 (3)	N40—C45	1.480 (3)
C5a—N5—C4	111.97 (15)	C35a—N35—C34	111.79 (16)
C10a—N10—C9	111.22 (15)	C40a—N40—C39	111.50 (15)
N5—C15—N10	113.19 (16)	N35—C45—N40	113.06 (16)
C4—N5—C5a—N6	79.2 (2)	C34—N35—C35a—N36	−78.9 (2)
C9—N10—C10a—N1	76.0 (2)	C39—N40—C40a—N31	−76.0 (2)
N2—N1—C18—C19	39.5 (3)	N32—N31—C48—C49	−36.1 (3)
N7—N6—C24—C29	19.3 (3)	N37—N36—C54—C59	−20.5 (3)

The aryl, methyl and methylenic H atoms were added at calculated positions and treated as riding with *SHELXL*97 (Sheldrick, 1997) defaults (C—H 0.93–0.97 Å) and were not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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