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3-(4-Chlorophenyldiazenyl)-1-methyl-2-phenyl-1*H*-indole

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.005 Å
R factor = 0.108
wR factor = 0.205
Data-to-parameter ratio = 19.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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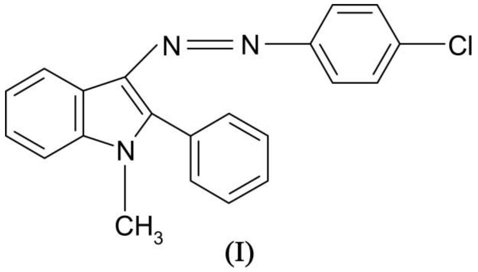
In the title compound, $C_{21}H_{16}ClN_3$, the asymmetric unit contains two crystallographically independent molecules. In each molecule, all of the rings are individually planar.

Comment

Azo derivatives are used extensively in analytical chemistry and in the dyestuff industry as metallochromic and acid–base indicators (Rau, 1990; Zollinger, 1987). They are also used in the fields of nonlinear optics and optical data storage (Clark & Hester, 1991; Bach *et al.*, 1996; Taniike *et al.*, 1996). Azo dyes have wide applicability as optical materials and so their structures have also attracted considerable attention (Biswas & Umapathy, 2000; Willner & Rubin, 1996). Indole and its derivatives form a class of toxic recalcitrant *N*-heterocyclic compounds that are considered as pollutants (Florin *et al.*, 1980; Ishiguro & Sugawara, 1978), and aryl azoindoles form yellow or orange dyes (Aldemir *et al.*, 2003). Many azo-dye breakdown products are carcinogenic, toxic or mutagenic to life (Ochiai *et al.*, 1986). Although there are many publications on the industrial applications of azo dyes (Tsuda *et al.*, 2000), to the best of our knowledge the structures of azoindole-type derivatives have not been reported to date. This study was undertaken in order to ascertain the crystal structure of the title phenyldiazenylindole dye, (I).



(I)

The asymmetric unit contains two crystallographically independent molecules, denoted by primed and unprimed labels (Fig. 1). The bond lengths and angles (Table 1) are in normal ranges (Allen *et al.*, 1987).

An examination of the deviations from the least-squares planes through individual rings shows that all of the rings are planar. The indole ring systems are nearly planar, with dihedral angles of $A/B = 1.56\ (11)^\circ$ and $A'/B' = 0.77\ (12)^\circ$ (rings are as defined in Fig. 1). Ring *B* has a local pseudo-mirror plane running through C6 and the mid-point of the N1—C8 bond, while ring *B*′ has a pseudo-twofold axis passing through C6′ and the mid-point of the N1′—C8′ bond, as evidenced by the torsion angles (Table 1). The orientations of the benzene rings

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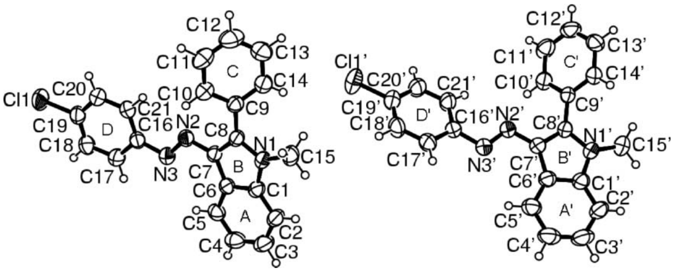

Figure 1
A drawing of the two-independent molecules of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

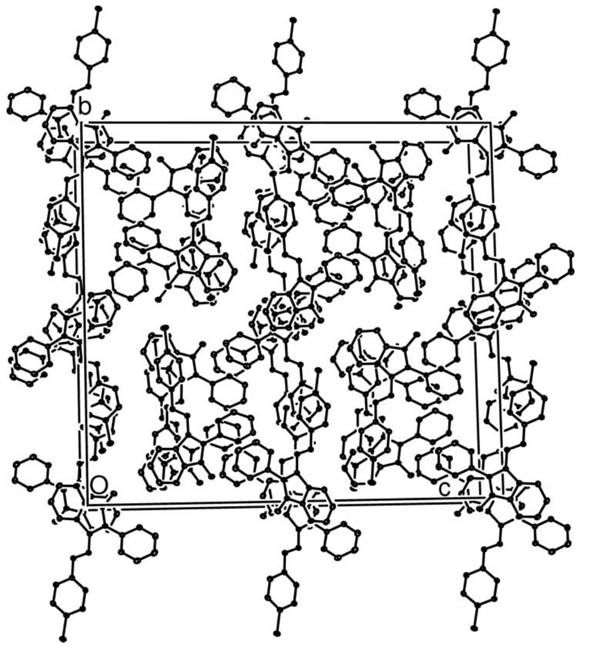

Figure 2
A packing diagram for (I), viewed down the *a* axis. H atoms have been omitted.

C, *D* and *C*′, *D*′ with respect to the indole ring systems in each molecule may be described by the dihedral angles of 43.45 (10) and 8.92 (10)°, and 46.85 (10) and 19.96 (8)°, respectively. The phenyldiazenyl unit of the unprimed molecule is planar, while it is not planar in the primed molecule, with a puckering amplitude Q_T = 0.275 (3) Å (Cremer & Pople, 1975).

As can be seen from the packing diagram (Fig. 2), the molecules of (I) are stacked along the *a* axis and elongated along the *b* axis. Dipole–dipole and van der Waals interactions are effective in the molecular packing.

Experimental

For the preparation of the title compound, 4-chloroaniline (0.28 g, 2 mmol) was dissolved in HCl (1.5 ml) and water (4.0 ml). The solution was cooled in an ice–salt bath and a cold solution of $NaNO_2$ (0.15 g, 2 mmol) in water (3.0 ml) was added dropwise with stirring. The resulting diazonium salt was also cooled in an ice–salt bath and then added dropwise with stirring to 1-methyl-2-phenylindole (0.41 g, 2 mmol) in an acetic acid–propionic acid mixture (8 ml, 2:1), cooled in a salt–ice bath. The solution was stirred at 273–278 K for 1 h and the pH of the reaction mixture was maintained at 4–6 by the simultaneous addition of solid sodium acetate (3–4 g) in portions. The mixture was stirred for a further 1 h. The resulting solid was filtered off, washed with cold water and recrystallized from ethanol (yield 0.63 g, 91%; m.p. 453 K).

Crystal data

$C_{21}H_{16}ClN_3$
M_r = 345.82
Orthorhombic, *Pcab*
a = 8.0836 (10) Å
b = 27.952 (4) Å
c = 30.483 (3) Å
V = 6887.7 (15) Å^3
Z = 16
D_x = 1.334 Mg m^{-3}
Mo *Kα* radiation
μ = 0.23 mm^{-1}
T = 296 (2) K
Rod, orange
0.35 × 0.20 × 0.10 mm

Data collection

Rigaku R-AXIS RAPID-S diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.924, T_{max} = 0.977
64891 measured reflections
10527 independent reflections
6382 reflections with $I > 2\sigma(I)$
R_{int} = 0.096
θ_{max} = 30.6°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.108
$wR(F^2)$ = 0.205
S = 1.18
10527 reflections
555 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0393P)^2 + 4.4415P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C8	1.375 (3)	N1′—C1′	1.395 (4)
N1—C1	1.391 (4)	N1′—C15′	1.455 (4)
N1—C15	1.462 (4)	N2′—C7′	1.385 (4)
N2—N3	1.277 (3)	N3′—N2′	1.272 (3)
N2—C7	1.385 (3)	N3′—C16′	1.428 (4)
N3—C16	1.422 (4)	C6′—C1′	1.402 (4)
C1—C6	1.406 (4)	C7′—C6′	1.440 (4)
C7—C8	1.391 (4)	C8′—N1′	1.372 (4)
C7—C6	1.440 (4)	C8′—C7′	1.392 (4)
C8—N1—C1	109.0 (3)	C8′—N1′—C1′	108.8 (3)
C8—N1—C15	127.9 (3)	C8′—N1′—C15′	126.6 (3)
C1—N1—C15	122.9 (3)	C1′—N1′—C15′	123.5 (3)
N3—N2—C7	114.3 (3)	N3′—N2′—C7′	114.8 (3)
N2—N3—C16	112.8 (3)	N2′—N3′—C16′	112.5 (3)
N2—C7—C6	131.1 (3)	N2′—C7′—C6′	131.9 (3)
N1—C8—C7	108.4 (3)	N1′—C8′—C7′	108.7 (3)
N1—C8—C9	122.8 (3)	N1′—C8′—C9′	123.0 (3)
C7—C8—C9	128.8 (3)	C7′—C8′—C9′	128.2 (3)
C1—N1—C8—C7	0.0 (3)	C8′—N1′—C1′—C6′	0.2 (4)
C8—N1—C1—C6	0.5 (3)	C7′—C6′—C1′—N1′	−0.1 (4)
N1—C1—C6—C7	−0.8 (3)	C8′—C7′—C6′—C1′	−0.1 (4)
C8—C7—C6—C1	0.8 (3)	C7′—C8′—N1′—C1′	−0.2 (4)
C6—C7—C8—N1	−0.5 (3)	N1′—C8′—C7′—C6′	0.2 (4)

Methyl H atoms were positioned geometrically, with C—H = 0.96 Å, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$. The remaining H atoms were located in a difference synthesis and refined isotropically [C—H = 0.90 (4)–1.00 (5) Å and

U_{iso}(H) = 0.0518 (8)–0.0810 (13) Å^2, and C′—H′ = 0.89 (3)–0.96 (3) Å and U_{iso}(H′) = 0.0518 (8)–0.0741 (12) Å^2].

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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