

## 4-[2-Methyl-4-(4-methylphenyldiazenyl)-phenoxy]phthalonitrile

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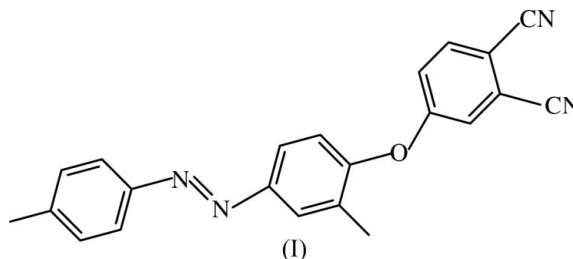
## Key indicators

Single-crystal X-ray study  
 $T = 296$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.053  
 $wR$  factor = 0.156  
Data-to-parameter ratio = 16.7For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}$ , displays a *trans* configuration with respect to the  $-\text{N}=\text{N}-$  double bond, as found for other diazene derivatives. There is a weak intramolecular  $\text{C}-\text{H}\cdots\text{N}$  hydrogen bond, which seems to have an effect on the molecular conformation. The crystal packing is governed by weak intermolecular  $\text{C}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds, and weak  $\text{C}-\text{H}\cdots\pi$  stacking.

## Comment

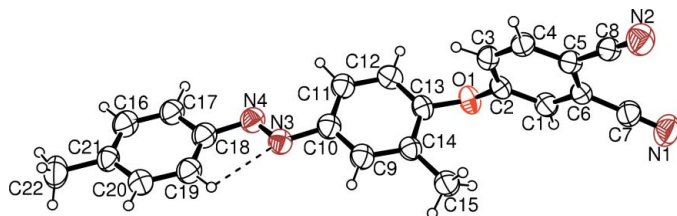
4-[2-Methyl-4-(4-methylphenyldiazenyl)phenoxy]phthalonitrile, (I), is a starting material in the synthesis of network polymeric phthalocyanines and high-performance aromatic polymers (McKeown, 1998; Takekoshi, 1987). In addition to their extensive use as dyes and pigments, phthalocyanines have found widespread applications in catalysis, optical recording, photoconductive materials, photodynamic therapy and as chemical sensors (Leznoff & Lever, 1989–1996).



Polymeric phthalocyanines have been known for their use as dyes and industrial high-technology materials and are also of additional interest because of their high thermostability (Leznoff & Lever, 1989–1996). Azo compounds have been the most widely used class of dyes owing to their versatile applications in various fields, such as dyeing textile fibres, colouring different materials, plastics, biological medical studies, lasers, liquid crystalline displays, electro-optical devices and ink-jet printers in high-technology areas (Catino & Farris, 1985; Gregory, 1991). The azo compound class accounts for 60–70% of all dyes. The geometric isomerism of azo compounds yields two forms, *viz.* *cis* and *trans*. A change from *trans* to *cis* can be effected by exposure to UV radiation, which can lead to photochromism. Photochromic compounds are of great interest for the control and measurement of radiation intensity, optical computers and display systems (Dürr & Bouas-Laurent, 1990). Photochromic materials of this type are of interest for potential applications in molecular electronic devices (Martin *et al.*, 1995), among others.

The molecular structure of (I) is shown in Fig. 1, with the atom-numbering scheme. Selected bond distances and angles are given in Table 1. The benzene rings C9–C14 and C16–C21

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**Figure 1**

An ORTEP-3 (Farrugia, 1997) drawing of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular hydrogen bond is indicated by a dashed line.

adopt *trans* configurations about the azo functional group, as observed in crystal structures of other azo compounds. The N3—C10 and N4—C18 bond lengths of 1.459 (3) and 1.449 (3) Å, respectively, indicate single-bond character, and the —N=N— bond length of 1.218 (3) Å is indicative of significant double-bond character. Similar values for corresponding bond distances and angles have been observed in related *trans*-azo compounds (Alder *et al.*, 1999, 2001; Dimmock *et al.*, 1997; Ersanlı *et al.*, 2004; Koşar *et al.*, 2004). The C7≡N1 and C8≡N2 bonds show N≡C triple bond character and are in good agreement with literature values (Ocak *et al.*, 2004; Devci *et al.*, 2004; Işık *et al.*, 2003). The dihedral angles between the mean planes of the C9—C14 and C16—C21 benzene rings and the C18—N4=N3—C10 azo bridge are 13.59 (9) and 33.3 (5)°, respectively. The C1—C2—O1—C13 and C10—N3—N4—C18 torsion angles are 145.4 (2) and −179.15 (18)°, respectively. The dihedral angles between rings *A* (C1—C6), *B* (C9—C14) and *C* (C16—C21) are *A/B* = 88.39 (6)°, *A/C* = 88.39 (6)° and *B/C* = 13.09 (14)°. The intramolecular C—H···N hydrogen bonds (Table 2) seem to affect the molecular conformation (Fig. 1). The molecules are linked by intermolecular C—H···N and C—H···O hydrogen bonds, and C—H···π interactions (Table 2), forming a three-dimensional network. The C19—H19···N3 hydrogen-bonded ring is coplanar with the adjacent ring, with a C19—C18—N4—N3 torsion angle of 0.32 (34) Å.

## Experimental

A mixture of 4-methylaniline (2.84 g, 26 mmol), water (50 ml) and concentrated hydrochloric acid (6.6 ml, 79 mmol) was stirred until a clear solution was obtained. This solution was cooled to 273–278 K and a solution of sodium nitrite (2.5 g, 36.4 mmol) in water was added dropwise while the temperature was maintained below 278 K. The resulting mixture was stirred for 30 min in an ice bath. *o*-Cresol (3.9 g, 36.4 mmol) solution (pH 9) was added gradually to a cooled solution of 4-methylbenzenediazonium chloride, prepared as described above, and the resulting mixture was stirred at 273–278 K for 60 min in an ice bath. The product was recrystallized from ethanol to obtain solid 2-methyl-4-(4-methylphenylazo)phenol (yield 84%, m.p. 441–443 K). To a solution of the solid (3.74 g, 16.5 mmol) in dimethylformamide (DMF) was added potassium carbonate (3.43 g, 33 mmol). The mixture was stirred for 30 min under N<sub>2</sub>. 4-Nitrophthalonitrile solution in DMF was added. The mixture was stirred for 48 h at 323 K under N<sub>2</sub> and poured into ice-water (150 g). The product was filtered off and washed with water. The product was recrystallized from

ethanol to obtain solid (I). Crystals of (I) were obtained from an ethanol/CCl<sub>4</sub> (1:2) mixture at room temperature by slow evaporation (yield 68%, m.p. 424–426 K).

## Crystal data

C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>O  
*M<sub>r</sub>* = 352.39  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 12.7084 (10) Å  
*b* = 8.0446 (9) Å  
*c* = 20.2971 (16) Å  
 β = 119.050 (5)°  
*V* = 1814.0 (3) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.290 Mg m<sup>−3</sup>  
 Mo Kα radiation  
 Cell parameters from 13869 reflections  
 θ = 1.8–27.9°  
 μ = 0.08 mm<sup>−1</sup>  
*T* = 296 K  
 Prism., brown  
 0.43 × 0.30 × 0.14 mm

## Data collection

Stoe IPDS-2 diffractometer  
 Rotation scans  
 Absorption correction: integration (*X-RED*; Stoe & Cie, 2002)  
*T<sub>min</sub>* = 0.964, *T<sub>max</sub>* = 0.990  
 17432 measured reflections  
 4285 independent reflections

1998 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.059  
 θ<sub>max</sub> = 27.8°  
*h* = −16 → 16  
*k* = −10 → 10  
*l* = −24 → 26

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.053  
*wR*(*F*<sup>2</sup>) = 0.157  
*S* = 0.91  
 4285 reflections  
 256 parameters

H atoms treated by a mixture of independent and constrained refinement  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0805*P*)<sup>2</sup>]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δσ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.40 e Å<sup>−3</sup>  
 Δρ<sub>min</sub> = −0.21 e Å<sup>−3</sup>

**Table 1**

Selected geometric parameters (Å, °).

C7—N1	1.138 (3)	C5—C8	1.431 (3)
C8—N2	1.143 (3)	C6—C7	1.432 (3)
C1—C6	1.380 (3)	C9—C14	1.383 (3)
C1—C2	1.380 (3)	C10—C11	1.387 (3)
C3—C4	1.382 (3)	C11—C12	1.388 (3)
C5—C6	1.399 (3)	C13—C14	1.393 (3)
		C18—C19	1.382 (4)
		C19—C20	1.386 (4)
C6—C1—C2	119.3 (2)	C17—C18—C19	119.3 (2)
C3—C2—C1	120.9 (2)	C21—C20—C19	121.1 (3)
C4—C5—C6	119.4 (2)	C20—C21—C16	117.4 (2)
C10—C9—C14	122.4 (2)	N4—N3—C10	113.1 (2)
C10—C11—C12	118.7 (2)	N3—N4—C18	111.7 (2)
C12—C13—C14	122.6 (2)	C2—O1—C13	117.82 (17)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C19—H19···N3	0.93	2.46	2.701 (3)	95
C15—H15A···N2 <sup>i</sup>	0.96 (3)	2.71 (3)	3.649 (4)	166 (2)
C17—H17···N2 <sup>ii</sup>	1.07 (3)	2.79 (3)	3.534 (4)	127 (2)
C22—H22A···O1 <sup>iii</sup>	0.96	2.90	3.684 (3)	140
C12—H12···Cg2 <sup>ii</sup>	0.90 (2)	3.03 (2)	3.796 (3)	144 (2)

Symmetry codes: (i) *x*, −*y* +  $\frac{3}{2}$ , *z* +  $\frac{1}{2}$ ; (ii) −*x*, *y* −  $\frac{1}{2}$ , −*z* +  $\frac{1}{2}$ ; (iii) −*x*, −*y* + 1, −*z* + 1. Cg2 is the centroid of ring *B* (C9—C14).

The H atoms of atoms C22 were positioned geometrically at a distances of 0.96 Å from the parent C atom; a riding model was used and *U*<sub>iso</sub>(H) values were constrained to be 1.5*U*<sub>eq</sub>(C). The other H

atoms were located in a difference Fourier map and refined freely [CH C–H = 0.88 (3)–1.07 (3) Å, CH<sub>3</sub> C–H = 0.94 (4)–0.97 (3) Å and  $U_{\text{iso}}(\text{H}) = 0.062$  (6)–0.114 (12) Å<sup>2</sup>].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); 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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