Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

2-(4-Methoxyphenylazo)-4-phenylphenol[1]

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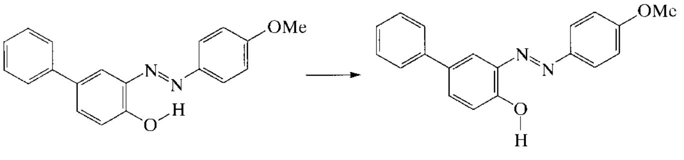
Received 23 March 2000
Accepted 15 May 2000

The crystal structure of the title compound, $C_{19}H_{16}N_2O_2$, displays a *trans* configuration of the azo moiety, which forms an intramolecular O—H···N═N hydrogen bond. The H···N and O···N distances are 1.81 (3) and 2.581 (4) Å, respectively. The azobenzene moiety is approximately planar, and has a dihedral angle of *ca* 23° with the substituted phenyl group.

Comment

The extensive application of azo dyes in industry and in analytical determinations has attracted attention for decades. Some arylazo compounds derived from resorcinol or β-naphthol have been widely used in the spectrophotometric determination of traces of metal (Betteridge & John, 1973; Pollard *et al.*, 1959). Furthermore, the tautomeric hydroxy-azoquinone–hydrazone equilibrium has been evidenced for this kind of compound (Stoyanov & Antonov, 1988; Antonov *et al.*, 1994, 1995; Antonov & Stoyanov, 1995; Buncel & Keum, 1983). The existence of the intramolecular hydrogen bond is of particular interest (Antonov & Stoyanov, 1995). Currently, we are developing a series of novel arylazo dyes derived from 4-phenylphenol in order to investigate the tautomeric equilibrium in solution. X-ray structure analysis of the title compound, (I), has been carried out to observe the conformation of the molecule in the crystal.



(I) (I*a*)

The molecular structure is shown in Fig. 1 with the atom-numbering scheme. The compound consists of phenyl rings *A* (C1 to C6), *B* (C11 to C16) and *C* (C17 to C22), and the azo frame *D* (C1—N1—N2—C12). The phenyl rings *A* and *B* adopt a *trans* configuration about the azo functional group, as observed in crystals of the other azo compounds. The dihedral angle between *A* and *B* is 2.7 (2)°, which is less than those in 3-*tert*-butyl-2′-chloro-2-hydroxy-5-methylazobenzene, (II) (5.85°; Işik, Aygün, Kocaokutgen & Tahir, 1998) and 2-hydroxy-5-*tert*-butylazobenzene, (III) (3.4°; Candan *et al.*, 1999). The phenyl-azo-benzene frame (*A*–*D*–*B*) is practically planar [shifts of the atoms from the best plane are less than 0.0341 (2) Å], as observed in the crystals of 3-*tert*-butyl-2-hydroxy-5-methoxyazobenzene, (IV) (Işik, Aygün, Kocaokutgen, Tahir *et al.*, 1998). The dihedral angles of ring *C* with ring *B* and the azo frame *D* are 24.2 (2) and 22.5 (2)°, respectively.

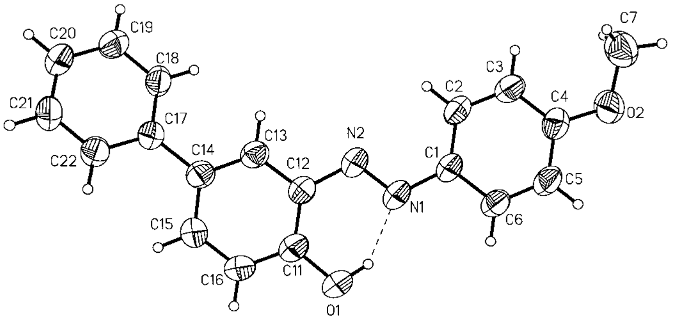


Figure 1
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The N1═N2 bond distance is 1.275 (2) Å (Table 1), which is longer than those observed in the azo compounds without intramolecular hydrogen bonds, 2-hydroxy-5-{[4-(2-pyridinylamino)sulfonyl]phenyl}azobenzoic acid [1.223 (7) Å; van der Sluis & Spek, 1990] and 5′-allyl-2′-benzoyloxy-3′-methoxy-4-nitroazobenzene [1.241 (3) Å; Işik *et al.*, 2000]. The lengthened N═N distance of (II) caused by the intramolecular hydrogen bond (Table 2) with the *ortho* hydroxyl group in the aromatic moiety is essentially identical to that of (IV), 1.274 (3) Å, and a little longer than those of (II) and (III), 1.266 (2) and 1.265 (2) Å, respectively. In bis(4-dimethylaminonaphthaleneazo)-4,4′-stilbene, the N═N distance is 1.256 (3) Å (Foitzik *et al.*, 1991). In (I), the C2—H2···N2 close contact [H2···N2 2.506 (3), C2···N2 2.762 (4) Å and C2—H2···N2 95.9 (2)°] may also contribute to the planarity of the molecule.

The intramolecular hydrogen bond in (I) is understandable when compared with another conformer, (I*a*), which can be derived from the concerted rotation of the O1—H1 bond of (I) around the C11—O1 axis by 180°. An *ab initio* calculation of the optimized geometries (Frisch *et al.*, 1993) indicated that the conformer (I) is more stable than (I*a*) by 56.4 and 42.5 kJ mol^{-1} at RHF/3–21G* and RHF/6–31G* levels, respectively.

Experimental

The title compound was prepared by azoic copulation of a 4-methoxyphenyldiazonium salt (0.022 mol of *p*-anisidine and 0.025 mol of sodium nitrite in strong acidic aqueous solution) with an

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[1] Dedicated to Professor Raúl Cetina-Rosado (1920–1999); contribution 1714 of the Instituto de Química, UNAM.

alkaline aqueous solution of 4-phenylphenol (0.021 mol). After chromatographic purification (hexane–ethyl acetate 70:30 in SiO_2 230–400 mesh), the crystals were grown by slow evaporation of the solution at room temperature (m.p. 396–399 K).

Crystal data

$C_{19}H_{16}N_2O_2$
$M_r = 304.34$
Monoclinic, $P2_1/n$
$a = 6.449$ (2) Å
$b = 8.638$ (2) Å
$c = 28.414$ (17) Å
$\beta = 90.48$ (4)°
$V = 1582.9$ (1) Å^3
$Z = 4$

$D_x = 1.277$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 49 reflections
$\theta = 4.9$–24.5°
$\mu = 0.084$ mm^{-1}
$T = 273$ (2) K
Prism, red
0.40 × 0.24 × 0.20 mm

Data collection

Siemens *P*4/*PC* diffractometer
ω–2θ scans
3062 measured reflections
2794 independent reflections
1126 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.045$
$\theta_{\rm max} = 25°$

$h = 0 \rightarrow 7$
$k = 0 \rightarrow 10$
$l = -33 \rightarrow 33$
3 standard reflections every 97 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.127$
$S = 0.767$
2794 reflections
212 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0102 (11)

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.361 (4)	N1—N2	1.275 (3)
O2—C4	1.360 (4)	N1—C1	1.423 (4)
O2—C7	1.414 (4)	N2—C12	1.409 (4)
N2—N1—C1	115.4 (3)	O2—C4—C3	125.6 (3)
N1—N2—C12	114.7 (3)	O1—C11—C16	118.8 (3)
C2—C1—N1	124.8 (3)	O1—C11—C12	121.8 (3)
C6—C1—N1	115.4 (3)	C11—C12—N2	126.3 (3)
O2—C4—C5	115.6 (3)	C13—C12—N2	115.3 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.88 (3)	1.81 (3)	2.581 (4)	146 (3)

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL*/*PC* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC*; software used to prepare material for publication: *SHELXL*97.

The authors wish to acknowledge PAEP UNAM for financial support, Dirección General de Cómputo Académico, UNAM for the supercomputer time on the Cray YMP464 and the indebted technical assistance of Héctor Ríos-Olivares, Carmen Campo-Garrido, Armando Noyola and Gabriela Magaña.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1031). Services for accessing these data are described at the back of the journal.

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