4-Hydroxy-ONN-azoxybenzene

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The oxidation of 4-hydroxyazobenzene provided a mixture of two azoxy compounds, which were separated by column chromatography. The isomer with the higher melting point appeared to belong to the α (ONN) series, as determined by X-ray diffraction. The molecule, $C_{12}H_{10}N_2O_2$, is almost planar. The benzene rings are twisted by 11.7 (2) (substituted) and 4.1 (1)° (unsubstituted) with respect to the ONN plane. The molecules are connected to one another by strong O—H···O hydrogen bonds forming chains extended along [001], which are bound by much weaker C—H···O hydrogen bonds forming layers in the bc plane.

Comment

The acid-catalysed transformation of azoxybenzenes into hydroxyazobenzenes is well known as the Wallach rearrangement. This is a simple aromatic, nucleophilic substitution reaction, with a remote leaving group (Shine, 1967). The nature of the symmetrical transition state is the subject of a controversy, since it has been found that either of the rings may be the migration terminus (Ozen *et al.*, 1998). The rearrangement of [15N]-azoxybenzene in a concentrated sulfuric acid gives equal amounts of the [15N]-4-hydroxyazobenzene molecules containing the tracer bound to the substituted and unsubstituted rings (Oae *et al.*, 1963). The result used to be rationalized in terms of a symmetrical intermediate (Buncel & Lawton, 1965; Shemyakin *et al.*, 1958). There are also some other possibilities which must be taken into consideration, *e.g.* that both aromatic rings in the protonated substrate molecules may be equally susceptible for the nucleophilic attack (Duffey & Hendley, 1968). Migration of the O atom from one nitrogen to another, during the rearrangement, may also interfere (Yamamoto *et al.*, 1982). In the case of unsymmetrical substituted azoxybenzenes, there is another possibility *viz* the structure of the substrate has not been established unequivocally.

The *para*-substituted azoxybenzenes seem to be interesting model compounds for investigations on the mechanism of the Wallach rearrangement, provided that their structures can be established beyond any doubt. We have prepared a large

series of these compounds. The isolation of both isomers, however, in the pure state was not possible in every case. It was found that the mass spectra of the compounds belonging to the α series are analogous and differ in some aspects from the spectra of β isomers. In the spectrum of (II*b*), the cleavage of the Ar—N bond plays an important role; the positive charge appears on both fragments, giving rise to the abundant peaks at m/z 121 and 93. They are absent in the spectrum of (II*a*), hence the isomeric series can be distinguished. The solution of which is the α and which is the β series requires the assistance of the X-ray diffraction method.

(1*a*) $X = Br$ (1*b*) $X = Br$
(II*a*) $X = OH$ (II*b*) $X = OH$
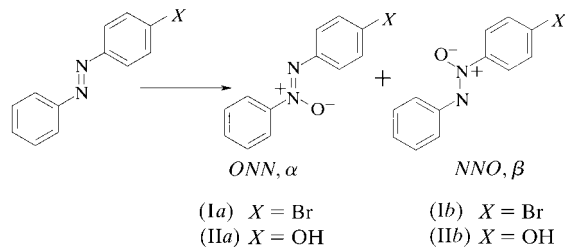
Selected geometrical parameters of compounds containing the azoxy group are presented in Table 3 for comparison. The experimental data (4-OH) are completed with the bond lengths and angles of azoxyanisole (Chebli & Brisse, 1995) and its homologue, 4,4'-di-*n*-propoxyazoxybenzene (Romain *et al.*, 1986), unsymmetrically substituted 4'-(*N,N*-dimethylamino)-azoxybenzene (Browning *et al.*, 1974) and *cis*-4'-methyl-azoxybenzene (Hoesch & Weber, 1977). Most azoxy compounds adopt the energetically more favourable *trans* conformation in the solid state. The only exception in the Cambridge Structural Database (CSD) is *cis*-4'-methylazoxy-benzene (Hoesch & Weber, 1977), which was added to Table 3 for comparison.

In the title compound, (II*a*) (Fig. 1), the N=N bond length is typical of the aromatic azo and azoxy compounds. The N—O distance (*ca* 1.26 Å) is shorter than in pyridine N-oxides (1.304 Å), but significantly longer than the N—O bond in the nitro group (1.218 Å) (Allen *et al.*, 1995). The *trans*-azoxy-benzenes are almost planar, whereas in the *cis* analogue the benzene rings are twisted *ca* ±56° with respect to the NNO plane. Such a conformation decreases the repulsion between the neighbouring groups. Generally, three planar fragments may be distinguished: the benzene ring connected to the N1 atom (*A*), the azoxy group (*B*) and the other benzene ring (*C*).
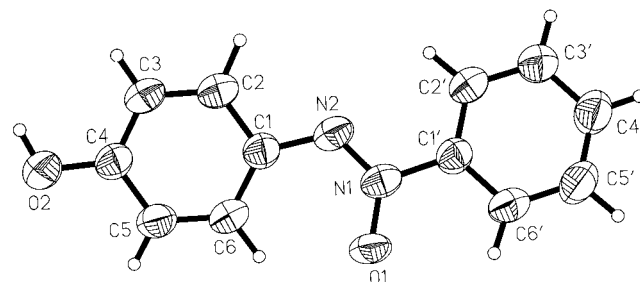

Figure 1
The molecular structure of 4-hydroxy-ONN-azoxybenzene. Displacement ellipsoids are shown at the 50% probability level.

The *A/B* angles in *trans*-azoxybenzenes are, in all cases, close to zero (Table 3). The other benzene ring (*C*) is systematically more twisted with respect to the azoxy group; the twist angle varies between *ca* 6 and 33° in all structures in the CSD, but only in a few cases does it exceed 10°.

In the molecular structure of the title compound some peculiarities are observed which cannot be explained at this stage of the investigation. The C1′—N1 bond is *ca* 0.04 Å longer than the analogous C1—N2 bond. The twist angle along the shorter bond is significantly greater [11.7 (2) *versus* 4.1 (1)°]. Such a deformation may result from the inter- and/or intramolecular interactions. The deformations from the planarity may also result from the steric hindrance around the azoxy group. The observations are not limited to the title compound; analogous geometry is characteristic of all the *trans* compounds listed in Table 3.

Another interesting feature is the geometry of the C1′—N1(O1)—N2—C1 group. The C1—N2—N1 angle together with C2′—C1′—N1 and C6′—C1′—N1 in *trans* azoxybenzenes are almost exactly equal to 120° as one would expect for the sp^2 hybridization. The N2—N1—O1 angle exceeds the expected value by 6°. The same holds true for C6—C1—N2, which is even larger. The same situation is observed for all *trans* azoxybenzenes. The enlargement of these angles may come from a repulsion between the NNO group and the aromatic ring bonded to the N2 atom. It should be noted, however, that the significant twist of the phenyl ring along the C1—N2 bond [*ca* 30° in the case of 4′-(*N,N*-dimethylamino)-azoxybenzene (Browning *et al.*, 1974)], which should minimize the repulsion, is not correlated with a significant decrease of the deformation of those angles. In the *cis* analogue we also
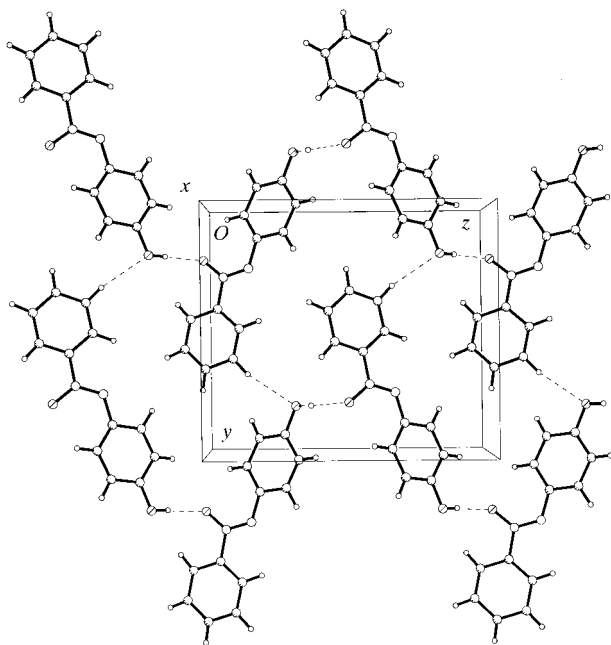
observe, although somewhat smaller, the increase of the C6—C1—N2 angle (*ca* 3°), whereas the N2—N1—O1 angle remains close to 120°. Instead, the C1′—N1—N2 angle is enlarged for *ca* 5°. This supports the supposition that the observed effects result from the intermolecular repulsion. In the case of *trans*-azoxybenzenes, the repulsion takes place between the N1—O1 group and the N2-bound phenyl ring, whereas in the case of the *cis* analogue, between two phenyl rings. An interesting feature is, however, that in both cases the deformation takes place on bonds centred on N1 and C1, whereas those centred on C1′ and N2 remain undisturbed.

The molecules are connected to one another with the O—H···O hydrogen bonds (Table 2) forming zigzag chains extended along the [001] axis. The *D*···*A* distance is less than the doubled van der Waals radius of the O atom, hence the hydrogen bond can be considered as a strong one. A weaker C—H···O interaction is responsible for the formation of layers in the *bc* plane (Fig. 2).

Experimental

Oxidation of 4-hydroxyazobenzene: 4-hydroxyazobenzene (7.93 g, 0.04 mol) was dissolved in acetic acid (120 ml). Hydrogen peroxide (40 ml of 30% H_2O_2) was added and the solution warmed in the boiling water bath for 3 h. It was poured into cold water (10 ml). A colloidal suspension was warmed to 353 K and slowly cooled. Yellow crystals (5.73 g, 67%) of the crude product were collected by filtration and dried in vacuum. They contained 27% of (II*a*) and 73% of (II*b*) according to the gas chromatography–mass spectrometry (GCMS) analyses. The isomers were separated on the column (Kieselgel) using a 1:1 benzene–*n*-heptane mixture and benzene as the eluents. The first fraction was crystallized twice from a 1:1 benzene–*n*-heptane mixture, yielding 4-hydroxy-*NNO*-azoxybenzene (1.83 g, 21%), (II*b*), as yellow crystals (m.p. 384.1–384.9 K). MS, *m/z* (int.): 214 (M^+, 100), 198 (6), 185 (44), 169 (13), 157 (1), 121 (52), 107 (85), 93 (19), 77 (61). ^{13}C NMR (DMSO-d_6, p.p.m.): 160.1 (C4), 143.8 (C1), 128.8 (C2) and 115.4 (C3, C atoms of the substituted ring), 139.6 (C7), 129.1 (C10), 124.7 (C11) and 124.0 (C12, C atoms of the unsubstituted ring). The second fraction was purified analogously providing 1.43 g (17%) of 4-hydroxy-*ONN*-azoxybenzene, (II*a*), as yellow needles (m.p. 429.3–429.8 K). The crystals of the second compound were suitable for the X-ray diffraction studies. The purity of the compound was 96% (high-pressure liquid chromatography) to 97% (GCMS). MS, *m/z* (int.): 214 (M^+, 100), 198 (5), 185 (8), 157 (3), 137 (4), 107 (43), 93 (11), 91 (8), 77 (95), 65 (12), 52 (31), 51 (24). ^{13}C NMR (DMSO-d_6, p.p.m.): 159.1 (C4), 136.1 (C1), 128.2 (C2) and 115.4 (C3, C atoms of the substituted ring); 147.7 (C7), 131.4 (C10), 128.0 (C11) and 121.7 (C12, C atoms of the unsubstituted ring).

Figure 2
The layers formed in the *bc* plane by molecules of 4-hydroxy-*ONN*-azoxybenzene connected to each other by O—H···O and C—H···O hydrogen bonds.

Crystal data

$C_{12}H_{10}N_2O_2$	D_m measured by flotation in a
$M_r = 214.22$	mixture of C_6H_6 and CCl_4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.187$ (1) Å	Cell parameters from 21
$b = 11.261$ (2) Å	reflections
$c = 12.812$ (3) Å	$\theta = 8$–11°
$V = 1036.9$ (3) Å^3	$\mu = 0.096$ mm^{-1}
$Z = 4$	$T = 293$ (2) K
$D_x = 1.372$ Mg m^{-3}	Plate, yellow
$D_m = 1.37$ (1) Mg m^{-3}	$0.5 \times 0.4 \times 0.3$ mm

Data collection

Kuma KM-4 diffractometer	$h = -10 \rightarrow 10$
ω–θ scans	$k = -15 \rightarrow 15$
2796 measured reflections	$l = -18 \rightarrow 18$
1729 independent reflections	2 standard reflections
1026 reflections with $I > 2\sigma(I)$	every 50 reflections
$R_{int} = 0.029$	intensity decay: 0.52%
$\theta_{max} = 30.13°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0252P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.1130P]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.993$	$(\Delta/\sigma)_{max} < 0.001$
1729 reflections	$\Delta\rho_{max} = 0.11$ e Å^{-3}
185 parameters	$\Delta\rho_{min} = -0.13$ e Å^{-3}
All H atoms refined isotropically	

Table 1
Selected geometric parameters (Å, °).

N2—N1	1.266 (3)	N1—C1′	1.453 (3)
N2—C1	1.402 (3)	O2—C4	1.351 (3)
N1—O1	1.284 (2)		
N1—N2—C1	121.5 (2)	C6—C1—N2	129.9 (2)
N2—N1—O1	126.1 (2)	O2—C4—C3	123.1 (2)
N2—N1—C1′	115.9 (2)	O2—C4—C5	117.8 (2)
O1—N1—C1′	118.0 (2)	C6′—C1′—N1	118.2 (2)
C2—C1—N2	112.1 (2)	C2′—C1′—N1	120.9 (2)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H22$\cdots$O1^i	0.85 (4)	1.88 (4)	2.722 (3)	170 (4)
C3′—H3′$\cdots$O2^{ii}	0.97 (3)	2.54 (3)	3.456 (3)	158 (3)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (ii) $x, y - 1, z$.

The C—H distance range is 0.91 (3)–1.05 (4) Å.

Data collection: *Kuma Diffraction Software* (Kuma, 1998); cell refinement: *Kuma Diffraction Software*; data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Table 3
Selected geometric parameters in some substituted azoxybenzenes (Å, °).

	4-OH	4,4′-(OMe)$_2$	4,4′-(OPr)$_2$	4′-N(Me)$_2$	*cis*-4′-Me
N1—N2	1.266 (3)	1.281	1.255	1.263	1.264
N1—O1	1.284 (2)	1.288	1.271	1.275	1.264
C1—N2	1.402 (3)	1.428	1.421	1.415	1.427
C1′—N1	1.453 (3)	1.445	1.475	1.442	1.470
C1′—N1—O1	118.0 (2)	118.9	115.7	114.6	114.3
C1′—N1—N2	115.9 (2)	116.5	116.0	118.4	125.0
N2—N1—O1	126.1 (2)	124.6	128.3	126.7	120.5
C1—N2—N1	121.5 (2)	120.6	118.8	118.8	119.2
C2—C1—N2	112.1 (2)	112.7	112.5	112.6	116.5
C6—C1—N2	129.9 (2)	127.5	130.0	127.8	123.4
C2′—C1′—N1	120.9 (2)	120.7	122.2	120.4	119.0
C6′—C1′—N1	118.2 (2)	119.5	117.2	119.8	118.3
A/B†	4.1 (1)	3.3	4.0	8.9	55.5
B/C	11.7 (2)	19.4	6.3	33.4	56.6
A/C	15.6 (1)	22.2	2.3	32.6	69.9

† The angle between the planes defined as: A the plane of the benzene ring connected to the atom N1; B the plane of the azoxy group; C the plane of the other benzene ring.

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