Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Orthorhombic polymorphs of two *trans*-4-aminoazoxybenzenes

Krzysztof Ejsmont, Małgorzata Broda, Andrzej Domański, Janusz B. Kyzioł and Jacek Zaleski*

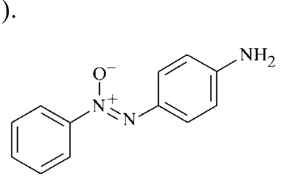
Institute of Chemistry, University of Opole, Oleska 48, 45-052 Opole, Poland
Correspondence e-mail: zaleski@uni.opole.pl

Received 27 May 2002
Accepted 5 July 2002
Online 10 August 2002

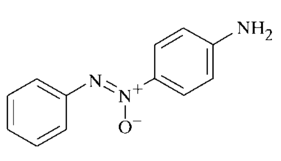
The two isomeric compounds 4-amino-*ONN*-azoxybenzene [or 1-(4-aminophenyl)-2-phenyldiazene 2-oxide], *i.e.* the α isomer, and 4-amino-*NNO*-azoxybenzene [or 2-(4-aminophenyl)-1-phenyldiazene 2-oxide], *i.e.* the β isomer, both $C_{12}H_{11}N_3O$, crystallized from a polar solvent in orthorhombic space groups, and their crystal and molecular structures have been determined using X-ray diffraction. There are no significant differences in the bond lengths and valence angles in the two isomers, in comparison with their monoclinic polymorphs. However, the conformations of the molecules are different due to rotation along the Ar—N bonds. In the α isomer, the benzene rings are twisted by 31.5 (2) and 14.4 (2)° towards the plane of the azoxy group; the torsion angles along the Ar—N bond in the β isomer are 24.3 (3) and 23.5 (3)°. Quantum-mechanical calculations indicate that planar conformations are energetically favourable for both isomers. The N—H···O hydrogen bonds observed in both networks may be responsible for the deformation of these flexible molecules.

Comment

The most effective method of preparation of azoxybenzene and its derivatives involves oxidation of the corresponding azobenzenes. The reaction is not regioselective and, consequently, an unsymmetrical substrate gives a mixture of the two isomers. The separation and identification of these isomers is difficult in most cases (Domański & Kyzioł, 2001); X-ray diffraction is the only reliable method for assigning the structure of a particular isomer. We have established the molecular and crystal structures of the monoclinic forms of the *NNO* and *ONN trans*-4-aminoazoxybenzenes (Domański *et al.*, 2001) but, in further experiments, the same compounds were obtained in different forms displaying higher melting points. Structural investigations revealed that the orthorhombic polymorphs of the isomers arise from crystallization using polar solvents, whereas the monoclinic polymorphs were obtained by crystallization from non-polar solvents. We present here the molecular and crystal structures of the orthorhombic polymorphs of 4-amino-*ONN*-azoxybenzene (α isomer), (I), and 4-amino-*NNO*-azoxybenzene (β isomer), (II).



α isomer, (I)



β isomer, (II)

The molecular structures of the title compounds are shown in Figs. 1(*a*) [α isomer, compound (I)] and 1(*b*) [β isomer, compound (II)]. The geometry of the bridge is nearly the same in both forms and both isomers. However, the N1—O1 bond is significantly longer (0.03 Å) in the orthorhombic form of the β isomer in comparison with the monoclinic form. Analogous differences are observed in the N1—N2 bond; these are limited to the β (*NNO*) isomer. The bonds between the bridge and the aromatic rings are of the same length in both isomers and both polymorphs. In all cases, the bond on the oxidized side of the bridge is *ca* 0.04 Å longer than that on the other side.

The valence angles are typical for the trigonal hybridization of the C and N atoms of the bridge. Some deviations (*e.g.* 128.2 *versus* 113.7°) are observed within the C—C—N angles on the unoxidized side of the azoxy group. Such a deformation results from steric interaction between atom O1 and the H atom in the *ortho* position.

There are typical features observed in the molecular structures of *trans*-azoxybenzenes (Domański *et al.*, 2001; Hoesch & Weber, 1977; Krigbaum & Barber, 1971; Krigbaum & Taga, 1974). There seems to be little evidence for the existence of C—H···O hydrogen bonds; the shortest O···H distances are 2.37 (2) and 2.34 (2) Å in (I), and 2.45 (2) and 2.25 (2) Å in (II). These distances are shorter than the sum of the van der Waals radii (2.6 Å) given by Pauling (1967).

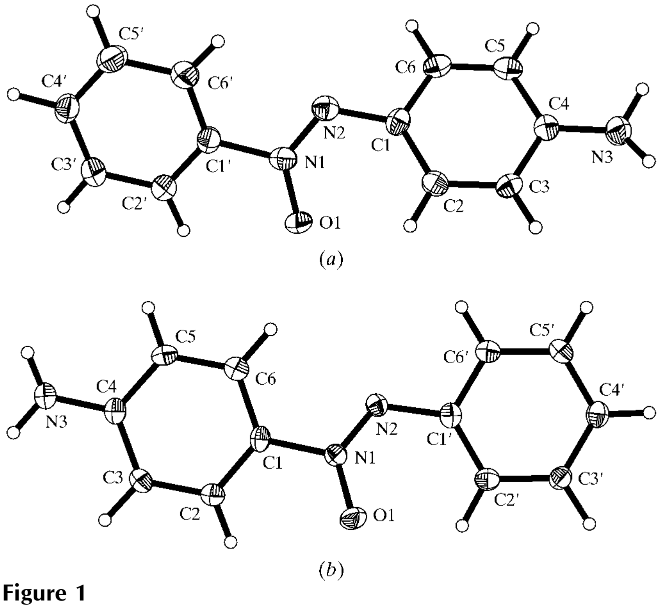


Figure 1
The molecular structure of (*a*) the α isomer, (I), and (*b*) the β isomer, (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270102011952

The sum of the valence angles around the amino N atom [*ca* 351° in (I) and 354° in (II)], and the distance of atom N3 from the C4/H31/H32 plane [0.18 (1) and 0.15 (1) Å for (I) and (II), respectively], indicate a lack of mesomeric interaction between the amino group and the aromatic ring. The planarity of the amino group has been analysed by two functions of the torsion angles, τ and χ_N (Ferretti *et al.*, 1993), defined as $\tau = (\omega_1 + \omega_2)/2$, characterizing the rotation around the C—N bond, and $\chi_N = \omega_2 - \omega_3 + \pi(\text{mode } 2\pi)$, which is a measure of the degree of pyramidalization of the N atom (where ω_1 = C5—C4—N3—H32, ω_2 = C3—C4—N3—H31 and ω_3 = C3—C4—N3—H32). These values are $\tau = 7°$ and $\chi_N = 35°$ in (I), and 1.5 and 29°, respectively, in (II). In both isomers, the χ_N values are intermediate between the extreme value for a regular tetrahedral sp^3 configuration (60°) and 0, corresponding to a planar sp^2 hybridization. In the monoclinic forms, the χ_N factor was bigger in the β isomer (46°) than in the α isomer (26°). It was inferred that the amino group situated on the unoxidized side of the azoxy bridge was more planar (Domański *et al.*, 2001). The dihedral angle between the amino group and the benzene ring is 28 (2)° in (I) and 23 (3)° in (II).

Three planar fragments in the molecular structure of these compounds may be distinguished, namely the benzene ring connected to atom N1 (*A*), the azoxy group (*B*) and the second benzene ring (*C*). In the α isomer, the dihedral angles between the various groups are *A*/*B* 13.6 (1), *B*/*C* 30.6 (1) and *A*/*C* 43.7 (1)°; the analogous values for the β isomer are 23.3 (2), 21.7 (2) and 1.8 (1)°, respectively. Additionally, the twists along the C_{aryl}—N bonds are illustrated by torsion angles of −31.5 (2) and −14.4 (2)° for the α isomer, and 24.3 (3) and −23.5 (3)° for the β isomer. These torsion angles are the most significant differences in the conformations of the molecules in the orthorhombic and monoclinic forms. Such conformations exclude effective conjugation between the amino and azoxy groups across the ring, which was suggested in our previous paper (Domański *et al.*, 2001). Steric hindrance around the azoxy group influences the conformations of the molecules, but intermolecular interactions within the crystal network seem to be important as well.

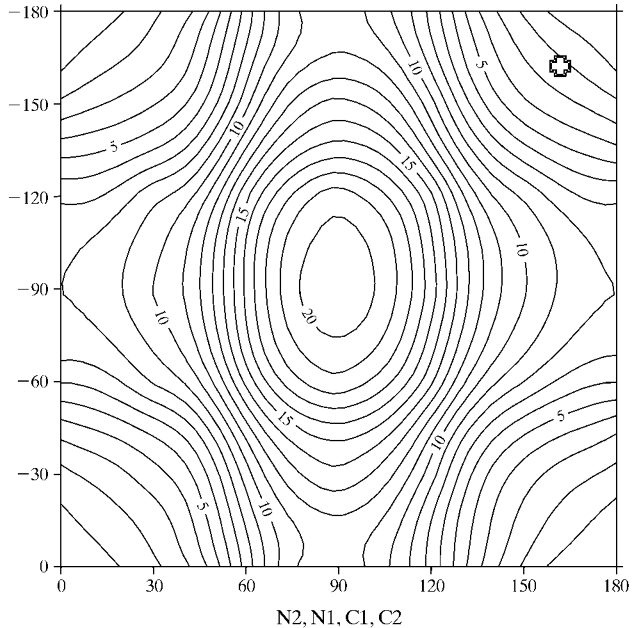
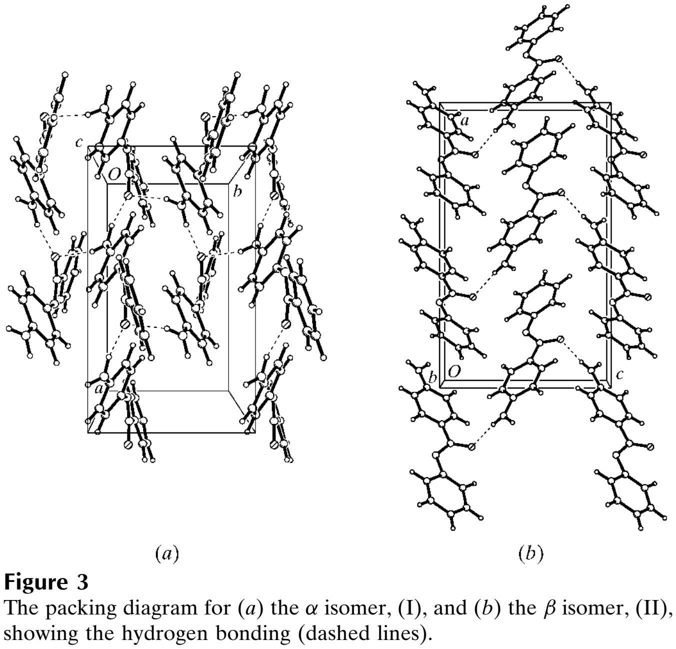


Figure 2
The conformational energy contour map of (II) as a function of the N2—N1—C1—C2 and N1—N2—C1′—C2′ torsion angles, obtained by the HF/3-21G method (Frisch *et al.*, 1998). Contours are labelled with energy in kcal mol^{-1} (1 kcal = 4.184 kJ) above the minimum energy point at (0°, 0°). The symbol in the upper right relates to the experimental conformation of (II) obtained from X-ray diffraction.

Azoxyarene molecules used to be considered as planar, and hence relatively large torsion angles along the Ar—N bonds were surprising. The results of quantum-mechanical calculations using the B3LYP/6-31G** method (Frisch *et al.*, 1998) are in agreement with this intuitive picture: planar conformations are the most stable for both isomers. The conformational energy contour map (Fig. 2) demonstrates that the conformation with both rings perpendicular to the azoxy bridge is the most unfavourable (20 kcal mol^{-1}; 1 kcal = 4.184 kJ). However, the deviations from planarity observed in the crystal network cause a total energy increase of 1.08 kcal mol^{-1} in (II) and 1.51 kcal mol^{-1} in (I). Consequently, the conformations of (I) and (II) in the orthorhombic and monoclinic networks may result from intermolecular interactions.

N—H···O hydrogen bonds are observed in both pairs of isomers. The molecular packing of the α and β isomers, with hydrogen bonds shown by dashed lines, is shown in Fig. 3. The IR spectra of the isomers are very similar in the high-wavenumber region, but the spectra of pairs of polymorphs are indistinguishable, *e.g.* 3447 and 3351 cm^{-1} *versus* 3447 and 3350 cm^{-1} in the case of the α isomer. The geometric parameters of the hydrogen bonds confirm the spectroscopic data. In both pairs, the interactions are weak and electrostatic in nature (Desiraju & Steiner, 1999). In spite of this, a closer approach of one molecule to another may cause deformation from the planar conformation in some cases.



(*a*) (*b*)

Figure 3
The packing diagram for (*a*) the α isomer, (I), and (*b*) the β isomer, (II), showing the hydrogen bonding (dashed lines).

Experimental

trans-4-(*N*-Acetylamino)azobenzene was oxidized with hydrogen peroxide in a mixture of acetic acid and acetic anhydride, as described by Domański *et al.* (2001). The crude product was hydrolysed and chromatographed. The homogenous fractions were evaporated to dryness and the residues were crystallized from methanol, providing crystals of (I) and (II) suitable for X-ray diffraction studies. The orthorhombic polymorphs were obtained by the above crystallization from methanol. When non-polar solvents were used, the monoclinic forms were obtained. The polymorphs of the isomers were examined by differential scanning calorimetry (DSC). The orthorhombic crystals contain no solvent molecules, although interactions with the solvent must have played an important role in growing the crystals. Their melting points, expressed as minima on the DSC curves, are higher (α 416.2–417.7 K and β 418.5 K) than those of the monoclinic polymorphs (α 408.9 K and β 407 K). Phase transitions of one polymorph into another were not observed.

Compound (I), α isomer

Crystal data

$C_{12}H_{11}N_3O$
$M_r = 213.24$
Orthorhombic, *Pbca*
$a = 12.058$ (2) Å
$b = 7.054$ (1) Å
$c = 24.398$ (5) Å
$V = 2075.2$ (6) Å^3
$Z = 8$
$D_x = 1.365$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3160 reflections
$\theta = 3.5$–$26.0°$
$\mu = 0.09$ mm^{-1}
$T = 90.0$ (2) K
Prism, orange
0.40 × 0.25 × 0.13 mm

Data collection

Kuma KM-4 diffractometer with a two-dimensional CCD area-detector
ω scans
12 684 measured reflections
2030 independent reflections

1617 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\rm max} = 26°$
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 6$
$l = -30 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.112$
$S = 1.11$
2030 reflections
191 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 0.1381P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N1—N2	1.268 (2)	N2—C1	1.406 (2)
N1—O1	1.282 (2)	C4—N3	1.367 (2)
N1—C1′	1.469 (2)		
N2—N1—O1	127.2 (1)	C6—C1—N2	113.7 (1)
N2—N1—C1′	115.4 (1)	N2—C1—C2	128.0 (1)
O1—N1—C1′	117.4 (1)	C6′—C1′—N1	121.0 (2)
N1—N2—C1	119.3 (1)	C2′—C1′—N1	117.8 (1)
N1—N2—C1—C6	154.0 (1)	N2—N1—C1′—C6′	−14.4 (2)
N1—N2—C1—C2	−31.5 (2)	N2—N1—C1′—C2′	166.1 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H31···O1$^{\rm i}$	0.92 (2)	2.19 (2)	3.083 (2)	165 (2)
N3—H32···O1$^{\rm ii}$	0.95 (2)	2.18 (2)	3.063 (2)	154 (2)

Symmetry codes: (i) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x - \frac{1}{2}, y, \frac{3}{2} - z$.

Compound (II), β isomer

Crystal data

$C_{12}H_{11}N_3O$
$M_r = 213.24$
Orthorhombic, $Pca2_1$
$a = 17.779$ (4) Å
$b = 5.535$ (1) Å
$c = 10.652$ (2) Å
$V = 1048.2$ (4) Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1630 reflections
$\theta = 3.7$–$25.5°$
$\mu = 0.09$ mm^{-1}
$T = 90.0$ K
Prism, yellow
0.25 × 0.14 × 0.12 mm

Data collection

Kuma KM-4 diffractometer with a two-dimensional CCD area-detector
ω scans
6087 measured reflections
1033 independent reflections

971 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\rm max} = 25.5°$
$h = -21 \rightarrow 21$
$k = -4 \rightarrow 6$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.067$
$S = 1.06$
1033 reflections
189 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.14$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

N1—O1	1.288 (2)	N2—C1′	1.427 (3)
N1—N2	1.292 (2)	N3—C4	1.381 (3)
N1—C1	1.469 (3)		
O1—N1—N2	127.9 (2)	C2—C1—N1	118.6 (2)
O1—N1—C1	116.5 (2)	C6—C1—N1	120.5 (2)
N2—N1—C1	115.6 (2)	C2′—C1′—N2	127.8 (2)
N1—N2—C1′	119.2 (2)	C6′—C1′—N2	112.3 (2)
N2—N1—C1—C2	157.9 (2)	N1—N2—C1′—C2′	24.3 (3)
N2—N1—C1—C6	−23.5 (3)	N1—N2—C1′—C6′	−159.9 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

*Cg*2 is the centroid of the unsubstituted ring C1′—C6′.

D—H···A	D—H	H···A	D···A	D—H···A
N3—H32···O1$^{\rm i}$	0.89 (3)	2.20 (3)	3.085 (3)	172 (3)
N3—H31···*Cg*2$^{\rm ii}$	0.91 (3)	2.56 (3)	3.357 (3)	146 (3)

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

Quantum-mechanical calculations were carried out using *GAUSSIAN*98 (Frisch *et al.*, 1998). Geometry optimization was performed using the Becke 3LYP density functional theory (DFT) hybrid method (Lee *et al.*, 1988; Becke, 1993) in combination with the 6-31G** basis set. The fully relaxed ($\Phi - \Psi$) conformational energy map *in vacuo* (30° spacing) of (II) was obtained by the HF (Hartree–Fock) method with the 3-21G basis set. H-atom coordinates were refined, giving C—H distances in the range 0.89 (3)–1.05 (1) Å and N—H distances in the range 0.89 (3)–0.95 (2) Å.

For both compounds, data collection: *KM*-4 *CCD Software* (Kuma, 1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD 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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1210). Services for accessing these data are described at the back of the journal.

References

Becke, A. D. (1993). *J. Chem. Phys.* **98**, 5648–5652.
Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, pp. 11–21. New York: Oxford University Press Inc.
Domański, A. A., Ejsmont, K., Kyzioł, J. B. & Zaleski, J. (2001). *Acta Cryst.* C**57**, 467–470.
Domański, A. A. & Kyzioł, J. B. (2001). *Pol. J. Chem.* **75**, 1839–1846.
Ferretti, V., Bertolasi, P., Gilli, P. & Gilli, G. (1993). *J. Phys. Chem.* **97**, 13568–13574.
Frisch, M. J. *et al.* (1998). *GAUSSIAN*98. Revision A3. Gaussian Inc., Pittsburgh, Pennsylvania, USA.
Hoesch, L. & Weber, H. P. (1977). *Helv. Chim. Acta*, **60**, 3015–3024.
Krigbaum, W. R. & Barber, P. G. (1971). *Acta Cryst.* B**27**, 1884–1891.
Krigbaum, W. R. & Taga, T. (1974). *Mol. Cryst. Liq. Cryst.* **28**, 85–98.
Kuma (1999). *KM*-4 *CCD Software*. Version 1.169. Kuma Diffraction, Wrocław, Poland.
Lee, C., Yang, W. & Parr, R. G. (1988). *Phys. Rev. B*: *Condens. Mat.* **37**, 785–789.
Pauling, L. C. (1967). *The Chemical Bond*, p. 152. Ithaca: Cornell University Press.
Sheldrick, G. M. (1990). *SHELXTL*. Siemens Analytical X-ray Instrument Inc., Madison, Winsconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.