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Received 31 July 2000

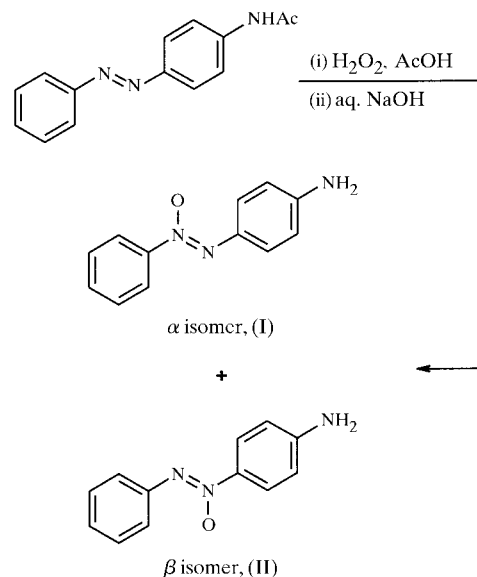
Accepted 4 January 2001

Two isomeric *trans*-4-aminoazoxybenzenes, *trans*-1-(4-amino-phenyl)-2-phenyldiazene 2-oxide ( $\alpha$ , C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O) and *trans*-2-(4-aminophenyl)-1-phenyldiazene 2-oxide ( $\beta$ , C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O), have been characterized by X-ray diffraction. The  $\alpha$  isomer is almost planar, having torsion angles along the C<sub>aryl</sub>–N bonds of only 4.9 (2) and 8.0 (2)°. The relatively short C<sub>aryl</sub>–N bond to the non-oxidized site of the azoxy group [1.401 (2) Å], together with the significant quinoid deformation of the respective phenyl ring, is evidence of conjugation between the aromatic sextet and the  $\pi$ -electron system of the azoxy group. The geometry of the  $\beta$  isomer is different. The non-substituted phenyl ring is twisted with respect to the NNO plane by *ca* 50°, whereas the substituted ring is almost coplanar with the NNO plane. The non-oxidized N atom in the  $\beta$  isomer has increased *sp*<sup>3</sup> character, which leads to a decrease in the N–N–C bond angle to 116.8 (2)°, in contrast with 120.9 (1)° for the  $\alpha$  isomer. The deformation of the C–C–C angles (1–2°) in the phenyl rings at the substitution positions is evidence of the different character of the oxidized and non-oxidized N atoms of the azoxy group. In the crystal structures, molecules of both isomers are arranged in chains connected by weak N–H...O ( $\alpha$  and  $\beta$ ) and N–H...N ( $\beta$ ) hydrogen bonds.

## Comment

We have recently (Ejsmont *et al.*, 2000) compared the structure of 4-hydroxy-*ONN*-azoxybenzene with some other *para*-substituted azoxybenzenes. We could not explain their molecular structures due to the diversity of substituents. Because of a lack of relevant structural data for the isomeric unsymmetrically substituted azoxybenzenes in the literature, we were prompted to prepare two isomeric *trans*-4-aminoazoxybenzenes and compare their geometries. We have selected amino derivatives since the amino group may be considered as a probe indicative of an intramolecular interaction of the azoxy group with the aromatic rings. Its influence on the amino group bonded to the ring, and on the oxidized and unoxidized sides of the azoxy bridge, should provide some information on the electronic properties of the azoxy group. The question is essential in investigations of the mechanism of the Wallach rearrangement. If the electron-withdrawing

properties of the azoxy group are applied to both rings, the proposal of Duffey & Hendley (1968) would seem to be reasonable. If not, the assumption of a symmetrical intermediate seems to be necessary (Buncel & Lawton, 1965). Another reason that *trans*-4-aminoazoxybenzenes are interesting subjects for structural investigation is their applicability to the syntheses of various derivatives of *trans*-azoxybenzene. Transformation or substitution of the amino group with another substituent can provide some *para*-substituted azoxybenzenes belonging to the same (ONN or NNO) series as the parent compound (Risaliti & Monti, 1961; Risaliti, 1963). This provides an opportunity to prepare isomers which are not accessible by the direct oxidation of azoxybenzenes, provided that the position of the amino group is unequivocally established. In our experience, polar substituents bound to the aromatic ring facilitate separation of the isomers. Consequently, we have oxidized 4-aminoazobenzene (protected with an *N*-acetyl group) to the corresponding title azoxybenzenes, separated the isomers to give compounds (I) ( $\alpha$  isomer) and (II) ( $\beta$  isomer), and examined their structures.

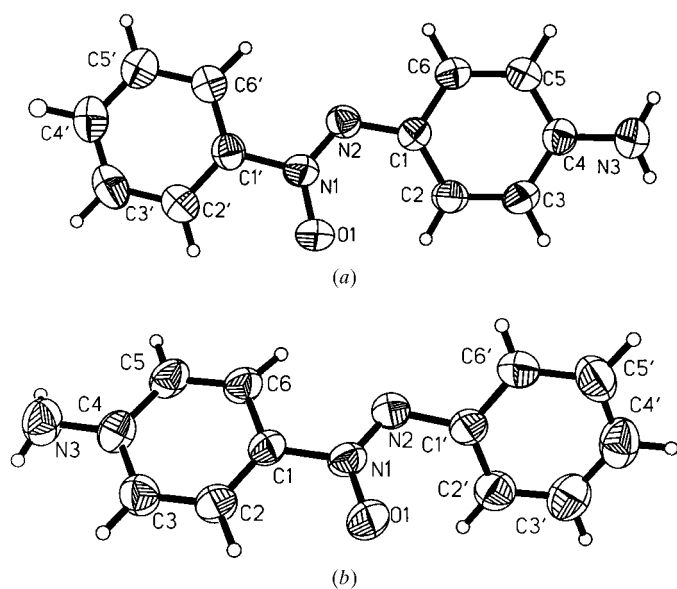


We have initially assumed that the azoxy group is an electron-withdrawing substituent, due to the formal positive charge on the oxidized N atom, analogous to the nitro group. The facts that the 4-nitroaniline molecule, the amino group and the aromatic ring lie in the same plane, and that the sum of the valence angles around the amino nitrogen is 360° indicate trigonal hybridization of the amino N atoms (Tonogaki *et al.*, 1993). On the other hand, in the 2-methyl-5-nitroaniline molecule, the amino group diverges from the ring plane and the sum of the angles about the amino nitrogen is less than 360° (Ellena *et al.*, 1999). Interaction of the complementary substituents across the ring depends on their relative positions. The aim of the present work is to answer the question of whether the azoxy group interacts with both aromatic rings in the same or a different way.

In the  $\beta$  isomer, (II) (Fig. 1), the sum of the valence angles around the amino nitrogen (*ca* 341°) and the distance of atom N3 from the C4/H32/H31 plane (0.25 Å) suggest a tetrahedral

configuration around the amino nitrogen. The internal coordinate  $\chi_N = (\text{H32}-\text{N3}-\text{C4}-\text{C3}) - (\text{H32}-\text{N3}-\text{C4}-\text{C5}) + \pi(\text{mod}2\pi)$ , which is a measure of the degree of nitrogen pyramidalization, is  $46^\circ$ . This is less than the extreme ( $60^\circ$ ) value for regular  $sp^3$  hybridization, but is much more than zero, which would indicate planar ( $sp^2$ ) geometry. The corresponding numbers for the  $\alpha$  isomer, (I), are as follows: the sum of the valence angles is *ca*  $354^\circ$ , the distance of N3 from the plane is  $0.14 \text{ \AA}$  and the factor  $\chi_N$  is  $26^\circ$ . It is inferred that the amino group situated on the unoxidized side of the azoxy bridge is more planar than in (II), but the deviation from regular  $sp^3$  hybridization is the same as in 2-methyl-5-nitroaniline (Ellena *et al.*, 1999). The lengths of the  $\text{C}_{\text{aryl}}-\text{NH}_2$  bonds [ $1.369(2) \text{ \AA}$  in (I) and  $1.385(3) \text{ \AA}$  in (II)] confirm that the interaction with the azoxy bridge is stronger in (I). It should be mentioned that a mesomeric interaction with the nitro group in a conjugated position shortens this bond to  $1.355 \text{ \AA}$  (Tonogaki *et al.*, 1993).

It can be expected that an interaction of the substituents across the ring will induce a quinonoid deformation of an aromatic hexagon. The effect is small, even in the case of 4-nitroaniline (Tonogaki *et al.*, 1993). In the present 4-amino azoxybenzenes, the average C—C bond length in the rings is  $1.379 \text{ \AA}$  and the deviations do not exceed  $0.01 \text{ \AA}$ , with one exception. In the substituted ring of (I), the bonds parallel to the N— $\text{C}_{\text{aryl}}$ —N axis are shorter (average  $1.370 \text{ \AA}$ ) than the remaining ones (average  $1.394 \text{ \AA}$ ). The effect is minute, but it is limited to one ring only, hence we can conclude that the amino group interacts with the azoxy substituent when the substituted ring is bound to the non-oxidized N atom. The conclusion seems to confirm the results obtained from the geometries of the amino groups. The interaction of the azoxy group with aromatic rings is of inductive character on one side and mesomeric on the other.



**Figure 1**  
The molecular structures of (a) the  $\alpha$  isomer (I) and (b) the  $\beta$  isomer (II). Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

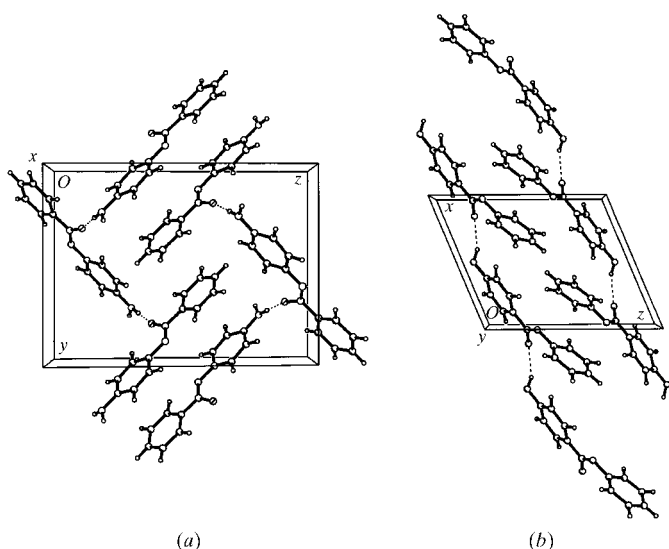
The character of the substituent on the benzene rings may be inferred by the relative change in the C—C—C bond angle at the *ipso* position. A decrease in this angle to below  $120^\circ$  is characteristic of an electron-releasing substituent (*ca*  $2^\circ$  in the case of aniline), whereas in the case of an electron acceptor bound to the ring, the angle is increased (*ca*  $3^\circ$  in the case of fluorobenzene; Domenicano, 1992). This effect is confirmed in the values of the  $\text{C3}-\text{C4}(-\text{NH}_2)-\text{C5}$  angles in both (I) and (II) (*ca*  $118^\circ$ ). It should be noted that the  $\text{C2}'-\text{C1}'-\text{C6}'$  angle in (I) is enlarged, as expected, to  $121.0(2)^\circ$ . The non-oxidized N atom bound to the other ring leads, however, to a decrease of the  $\text{C2}-\text{C1}-\text{C6}$  bond angle to  $117.7(2)^\circ$ . This influence is almost the same as in the case of the  $\text{NH}_2$  group. It seems to affirm that the character of the N atoms (non-oxidized and oxidized) is different. In the case of (II), the  $\text{C6}-\text{C1}-\text{C2}$  angle remains almost the same as the respective angle in (I), whereas the  $\text{C6}'-\text{C1}'-\text{C2}'$  angle is only slightly smaller than  $120^\circ$ . The deformation is most probably much smaller due to the twist of this phenyl ring with respect to the NNO plane, which prevents conjugation.

In the *trans*-azoxybenzenes, the benzene ring bound to the oxidized site of the azoxy bridge is almost always coplanar with it, irrespective of the substituent present (Ejsmont *et al.*, 2000, and references therein). While the reason for this is not clear, it may result from the interaction of the O atom of the NNO group with the ring bound to the oxidized N atom. On the other hand, the other phenyl ring shows a much larger tendency to become twisted with respect to the NNO plane. The geometry of the azoxy group in (I) and (II) is consistent with such a picture. In both isomers, the N—N,  $\text{C}_{\text{aryl}}-\text{NO}$  and N—O bonds have typical lengths (Ejsmont *et al.*, 2000), although the latter are slightly shorter. The differences between the  $\text{C}_{\text{aryl}}-\text{NO}$  and  $\text{C}_{\text{aryl}}-\text{N}$  bond lengths are observed in both isomers, with the  $\text{C}_{\text{aryl}}-\text{N}$  bond always shorter. The most significant difference between (I) and (II) is the conformation of the rings with respect to the NNO plane. In (II), the unsubstituted ring is significantly twisted along the  $\text{C}_{\text{aryl}}-\text{N}$  bond [torsion angles  $54.6(3)$  and  $134.9(2)^\circ$  measured to both *ortho*-C atoms]. The twist of the benzene ring with respect to the NNO plane is associated with an increase of the  $\text{C}_{\text{aryl}}-\text{N}$  bond length [ $1.420(3) \text{ \AA}$  in (II) compared with  $1.401(2) \text{ \AA}$  in (I)]. It also increases the  $sp^3$  character of the non-oxidized N atom [ $\chi_N$  factor of  $9.6^\circ$  in (II) compared with a  $\chi_N$  value of  $0.4^\circ$  in (I)]. This is confirmed by the relative shift of atom H6 in (II), which interacts with the lone pair on N2. This leads to an increase of the  $\text{C5}-\text{C6}-\text{H6}$  angle to  $125(1)^\circ$  and a decrease of the  $\text{C1}-\text{C6}-\text{H6}$  angle to  $116(1)^\circ$ . The respective angles in (I) are  $120(1)$  and  $118(1)^\circ$ . The twist does not result from steric hindrance around the O atom. The distances to H atoms in the *ortho* positions are  $2.36 \text{ \AA}$  in the coplanar ring and  $2.63 \text{ \AA}$  in the twisted ring.

The geometry of the  $\alpha$  isomer, (I), is different; the molecule is essentially planar, so the torsion angles along the  $\text{C}_{\text{aryl}}-\text{N}$  bonds are only  $4.8(2)$  and  $8.0(2)^\circ$ . The conjugation between the aromatic sextet and the  $\pi$ -electron system of the azoxy group bound to the non-oxidized N atom cannot be excluded, especially if one takes into account the shortening of the

C2—C3 and C5—C6 bonds with respect to the others of the same phenyl ring. The increase in the N—N—O angle to 126.4 (1)° and the N2—C1—C2 angle to 129.7 (1)° brings the H2···O1 distance to 2.18 Å, compared with an H2'···O1 distance of 2.39 Å. The H2···O1 distance is rather short and must result in a significant repulsion between the atoms in question. In spite of that, the monosubstituted benzene ring remains almost coplanar with the azoxy group. We may therefore conclude that the inductive/mesomeric interactions of the non-oxidized N atom of the NNO group and the N atom of the amino group are energetically more favourable than the repulsion interactions between the O atom of the NNO group and the phenyl ring.

Intermolecular interactions contribute significantly to the crystal structures of the compounds under discussion. In particular, N—H···O or N—H···N hydrogen bonds are expected. The FT-IR spectra of the  $\alpha$  and  $\beta$  isomers are very similar; in the region of  $\nu > 3000 \text{ cm}^{-1}$ , two peaks (see *Experimental*) characteristic of the primary amino group are observed. In the spectra registered in chloroform solutions, the absorption bands at 3503 and 3410  $\text{cm}^{-1}$  for (I), and 3504 and 3411  $\text{cm}^{-1}$  for (II), obey the rule  $\nu_{\text{asym}} = 0.876\nu_{\text{sym}} + 345.5$ , indicating the presence of free amino groups. In the spectra registered in KBr pellets, these maxima are shifted toward lower wave numbers by *ca* 60  $\text{cm}^{-1}$ , *i.e.* by only about 2%. According to the Desiraju & Steiner (1999) classification of hydrogen bonds, such spectral characteristics of this interaction indicate that it is weak ( $< 4 \text{ kcal mol}^{-1}$ ; 1 cal = 4.184 J). When H···O distances are greater than 2.0 Å they are of electrostatic character (Desiraju & Steiner, 1999). The present X-ray diffraction studies confirm the spectroscopic data. The molecular packing of the  $\alpha$  and  $\beta$  isomers is shown in Fig. 2. The molecules are arranged in chains connected to each other by weak N—H···O [in (I) and (II)] and N—H···N [in (II)] hydrogen bonds.



**Figure 2**  
The packing diagram of (a) the  $\alpha$  isomer (I) and (b) the  $\beta$  isomer (II), showing the hydrogen-bonding (dashed lines).

## Experimental

To prepare 4-aminoazoxybenzene, 4-(*N*-acetylamino)azobenzene (9.57 g, 0.040 mol) was dissolved in a mixture of acetic acid (100 ml) and acetic anhydride (30 ml). To the stirred solution, hydrogen peroxide (30%, 40 ml) was added and the mixture was stirred for 4 h at 323 K. It was then poured onto ice, and a yellow precipitate was collected by filtration and dried. The crude product was dissolved in ethanol (300 ml), sodium hydroxide (4.80 g, 0.12 mol) was added as a concentrated aqueous solution and the mixture was stirred under reflux for 2 h. It was then concentrated and poured onto ice. A yellow precipitate (7.41 g, 87%) was collected by filtration and dried. It was a mixture of equal amounts of both isomers, (I) and (II) (m.p. 375–383 K), contaminated with small amounts of the substrate, as indicated by high-performance liquid chromatography (HPLC) analyses. To prepare the  $\beta$  isomer, (II), the aforementioned product (1.00 g) was dissolved in benzene (20 ml) and chromatographed on a column with silica gel, using a benzene–*n*-heptane mixture (1:1, *v/v*) as the eluent. The substrate was eluted first and the next fraction (0.34 g) contained mainly (73%, HPLC) compound (II). This was crystallized twice from the same solvent yielding (II) (0.15 g) as yellow needles melting at 410.6–411.5 K (differential scanning calorimetry, onset 406 K,  $\delta H = 33 \text{ kJ mol}^{-1}$ ). Spectroscopic analysis: MS, *m/z* (intensity): 213 ( $M^+$ , 65), 185 (17), 121 (28), 106 (77), 92 (100), 77 (21), 65 (62);  $^{13}\text{C}$  NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , p.p.m.): 152.8 (C4), 144.2 (C1'), 136.2 (C1), 128.3 (C4'), 112.5 (C3), 128.7, 124.5 and 123.7 (remaining C atoms); IR (KBr,  $\text{cm}^{-1}$ ): 3441, 3333 (stretching vibrations of the  $\text{NH}_2$  group), 1629 (amino group deformations), 1460, 1324 (N—O and N=N stretching vibration within the azoxy group). To prepare the  $\alpha$  isomer, (I), the last fraction from the column was collected. This provided orange crystals (0.52 g) of (I) (88% purity according to HPLC). After repeated crystallization, pure (I) (0.32 g) was obtained (m.p. 411–412.3 K; differential scanning calorimetry, onset 404 K,  $\delta H = 28 \text{ kJ mol}^{-1}$ ). Spectroscopic analysis: MS, *m/z* (intensity): 213 ( $M^+$ , 80), 121 (2), 106 (100), 92 (10), 77 (33), 65 (10);  $^{13}\text{C}$  NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , p.p.m.): 151.4 (C4), 147.7 (C1'), 133.3 (C1), 130.6 (C4'), 112.9 (C3), 129.0, 128.3 and 121.3 (remaining aromatic C atoms); IR (KBr,  $\text{cm}^{-1}$ ): 3447, 3351 (primary amino group), 1632 (deformations of the amino group), 1472, 1317 (asymmetric and symmetric stretch of the azoxy group).

## Compound (I)

### Crystal data

$\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}$   
 $M_r = 213.24$   
Monoclinic,  $P2_1/n$   
 $a = 5.733$  (1) Å  
 $b = 11.602$  (2) Å  
 $c = 16.038$  (3) Å  
 $\beta = 93.16$  (3)°  
 $V = 1065.1$  (3) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.330 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
Cell parameters from 28 reflections  
 $\theta = 8\text{--}13^\circ$   
 $\mu = 0.089 \text{ mm}^{-1}$   
 $T = 293$  (2) K  
Prism, orange  
 $0.7 \times 0.6 \times 0.2 \text{ mm}$

### Data collection

Kuma KM-4 diffractometer  
 $\omega/\theta$  scans  
4164 measured reflections  
1888 independent reflections  
1480 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 25.05^\circ$

$h = -6 \rightarrow 6$   
 $k = -13 \rightarrow 0$   
 $l = -19 \rightarrow 19$   
2 standard reflections  
every 50 reflections  
intensity decay: 0.67%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.101$   
 $S = 1.033$   
 1888 reflections  
 190 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0736P)^2 + 0.1764P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I).

O1—N1	1.268 (2)	N2—C1	1.401 (2)
N1—N2	1.261 (2)	N3—C4	1.369 (2)
N1—C1'	1.456 (2)		
N2—N1—O1	126.4 (1)	C6—C1—N2	112.7 (1)
N2—N1—C1'	116.3 (1)	C2—C1—N2	129.7 (1)
O1—N1—C1'	117.2 (1)	C6'—C1'—N1	120.7 (1)
N1—N2—C1	120.9 (1)	C2'—C1'—N1	118.2 (1)
N1—N2—C1—C6	−171.8 (1)	N2—N1—C1'—C6'	−5.2 (2)
N1—N2—C1—C2	7.8 (2)	N2—N1—C1'—C2'	174.5 (1)

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H31 $\cdots$ O1 <sup>i</sup>	0.88 (2)	2.13 (2)	2.999 (2)	171 (2)

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

Compound (II)

Crystal data

$C_{12}H_{11}N_3O$   
 $M_r = 213.24$   
 Monoclinic,  $P2_1$   
 $a = 8.764 (2) \text{ \AA}$   
 $b = 6.103 (1) \text{ \AA}$   
 $c = 10.791 (2) \text{ \AA}$   
 $\beta = 112.97 (3)^\circ$   
 $V = 531.4 (2) \text{ \AA}^3$   
 $Z = 2$

$D_x = 1.333 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 8-12^\circ$   
 $\mu = 0.089 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prism, yellow  
 $0.6 \times 0.4 \times 0.4 \text{ mm}$

Data collection

Kuma KM-4 diffractometer  
 $\omega/\theta$  scans  
 2506 measured reflections  
 1432 independent reflections  
 973 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\max} = 30.05^\circ$

$h = -11 \rightarrow 11$   
 $k = -7 \rightarrow 7$   
 $l = -11 \rightarrow 15$   
 2 standard reflections every 50 reflections  
 intensity decay: 0.03%

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.031$   
 $wR(F^2) = 0.096$   
 $S = 1.044$   
 1432 reflections  
 189 parameters  
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0472P)^2 + 0.0451P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.081$   
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$

Table 3

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

O1—N1	1.257 (3)	N2—C1'	1.421 (3)
N1—N2	1.266 (3)	N3—C4	1.385 (3)
N1—C1	1.450 (3)		
O1—N1—N2	125.6 (2)	C2—C1—N1	118.5 (2)
O1—N1—C1	116.9 (2)	C6—C1—N1	120.5 (2)
N2—N1—C1	117.5 (2)	C2'—C1'—N2	122.4 (2)
N1—N2—C1'	116.8 (2)	C6'—C1'—N2	117.1 (2)
O1—N1—N2—C1'	7.7 (3)	N2—N1—C1—C6	−2.1 (3)
O1—N1—C1—C2	−4.7 (3)	N1—N2—C1'—C2'	54.6 (3)
N2—N1—C1—C2	175.9 (2)	N1—N2—C1'—C6'	−134.9 (2)

Table 4

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H32 $\cdots$ O1 <sup>ii</sup>	0.96 (3)	2.09 (3)	2.918 (3)	143 (3)
N3—H31 $\cdots$ N3 <sup>iii</sup>	0.79 (3)	2.68 (3)	3.432 (2)	161 (3)

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

Refined C—H distances were in the range 0.93 (2)–0.99 (2)  $\text{\AA}$  for the  $\alpha$  isomer (I) and in the range 0.87 (2)–0.98 (3)  $\text{\AA}$  for the  $\beta$  isomer (II).

For both compounds, data collection: *Kuma Diffraction Software* (Kuma, 1998); cell refinement: *Kuma Diffraction Software*; data reduction: *Kuma Diffraction Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1152). Services for accessing these data are described at the back of the journal.

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