

Double anomeric effects and a hydrogen-bonded supramolecular motif in *N,N'*-bis(3-nitrophenyl)-methanediamine

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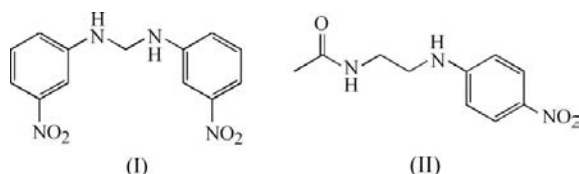
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In the title compound, $C_{13}H_{12}N_4O_4$, the molecule lies on a crystallographic twofold axis. Molecules are linked into complex sheets parallel to (100) via one $N-H\cdots O$ and two $C-H\cdots O$ hydrogen bonds. Within the molecule, the 3-nitroanilino fragment is essentially planar, and the $C-N-C-N$ fragment assumes a nearly perpendicular/perpendicular conformation, with $C-N-C-N$ torsion angles of 81.18 (18°), which is controlled by a pair of adjacent anomeric interactions. The findings constitute the first demonstration of two anomeric effects existing in one $N-C-N$ unit.

Comment

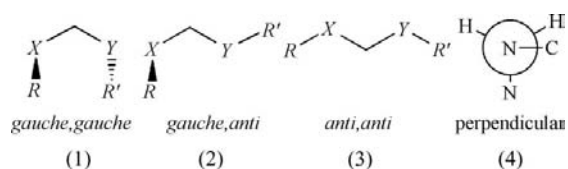
The reactions (Michael *et al.*, 1997; Layer, 1963) of aliphatic aldehydes with primary amines or ammonia may yield hemiaminals, some of which can be stabilized by electron-withdrawing substituent(s), such as a trichloromethyl group. However, those formed from aliphatic amines subsequently dehydrate to give imines. The imines formed from primary amines are prone to dimerization, polymerization or addition reactions with excess aniline (Michael *et al.*, 1997; Layer, 1963; Zhang, Wang *et al.*, 2007; Zhang, Qin *et al.*, 2007).



Recently, it was found that the condensation of formaldehyde with anilines carrying strong electron-withdrawing groups proceeded smoothly to afford *N,N'*-bisphenylmethanediamines (Kibayashi & Yamazaki, 2007). This suggests that the imines formed from primary amines carrying strong electron-withdrawing substituents are prone to nucleophilic addition reactions with anilines. However, our interest here lies in exploring the anomeric effect(s) in the

$C-NH-CH_2-NH-C$ fragment of the title compound, (I).

The anomeric effect plays an important role in controlling the molecular conformation in systems containing geminal heteroatoms (Juaristi & Cuevas, 1992). The term 'anomeric effect' generally refers to the preferred torsion angles between the $R-X$ and $C-Y$ bonds in the $R-X-CH_2-Y-R'$ fragments. The conformations increase in energy in the sequence *gauche,gauche* (1) < *anti,gauche* (2) < *anti,anti* (3) (see scheme below). The torsion angle, bond-length variations and bond-angle variations in $R-X-CH_2-Y-R'$ fragments have been rationalized both qualitatively (David *et al.*, 1973; Pinto *et al.*, 1985) and quantitatively (Wolfe *et al.*, 1979) by a perturbational molecular orbital treatment that focuses on the stabilizing orbital interactions between the p -type nonbonding orbitals on X and Y , viz. $n(X)$ and $n(Y)$, with the acceptor orbitals, viz. $\sigma^*(C-X)$ and $\sigma^*(C-Y)$, respectively. Whereas both such interactions may operate in (1), symmetry considerations imply that only one such interaction, such as $n(X) \rightarrow \sigma^*(C-Y)$, is possible in (2), and neither interaction is possible in (3). These hyperconjugative interactions account for the existence of the anomeric effects.



If we concentrate on the anomeric effect in $C-N-C-N$ fragments, crystallographic analyses have confirmed that each such unit adopts a nearly perpendicular/*anti* conformation (see scheme immediately above), where one $C-N-C-N$ torsion angle is close to 90° and the other is close to 180° , and that there is only one $n(N) \rightarrow \sigma^*(C-N)$ interaction determining the conformation (Zhang, Wang *et al.*, 2009; Zhang, Zhang *et al.*, 2009; Kakanejadifard & Farnia, 1997). While the existence of this conformational effect in $N-C-N$ systems has been widely accepted, the interesting conformational characteristics of the title compound have

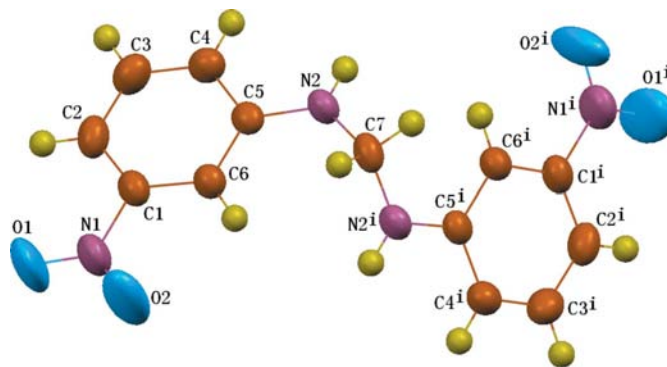


Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$]

attracted our attention. We report here the results of our investigation of the anomeric effect and hydrogen-bonded supramolecular structure of (I) (Fig. 1).

The molecule of (I) lies on a crystallographic twofold axis. The 3-nitroanilino fragment is essentially planar. The nitro group is slightly twisted out of the plane of the benzene ring, and also exhibits significant thermal motion. Interestingly, unlike the reported C–N–C–N–C units with a nearly perpendicular/*anti* conformation (Zhang, Wang *et al.*, 2009; Zhang, Zhang *et al.*, 2009; Kakanejadifard & Farnia, 1997), the C–N–C–N–C fragment here assumes a nearly perpendicular/perpendicular conformation (Fig. 1); the C5–N2–C7–N2ⁱ torsion angle and its symmetry-related counterpart [symmetry code: (i) $-x, y, -z + \frac{1}{2}$] are 81.18 (18)°, thus allowing the N2 *p*-orbital to hyperconjugate with the C7–N2ⁱ σ^* antibonding orbital, with commensurate shortening of the C7–N2 bond. This conformation for the C5–N2–C7–N2ⁱ–C5ⁱ unit is very similar to those found in the structures of *N,N'*-bis(2-nitrophenyl)methanediamine, 3-(((tert-butoxycarbonyl)amino)methyl)amino)-2,2-dimethyl-3-oxopropanoic acid and 2,2'-dimethyl-7,7'-(methylenediimino)di-1,8-naphthyridin-1-ium bis(perchlorate), where the corresponding torsion angles lie in the range 74.2–90.3° (Hanson, 1980; Crisma *et al.*, 2007; Mo *et al.*, 2008). The marked torsion-angle preference is just a striking expression of two anomeric effects acting in the N2–C7–N2ⁱ fragment. This can be further confirmed by some correlative geometric parameters (Table 1). In the NH–CH₂–CH₂–NH fragment of *N*-{2-[(4-nitrophenyl)amino]ethyl}acetamide, (II) (Wang *et al.*, 2004), anomeric interactions are not possible and the N atoms have a similar chemical environment and identical hybridization (*sp*²) to those of atoms N2 and N2ⁱ of the title compound; in (II), the N–CH₂ bond lengths [1.456 (3) and 1.459 (3) Å] are consistent with the usual values for *Nsp*²–CH₂ bonds (1.452–1.459 Å; Yonkey *et al.*, 2008; Walczak *et al.*, 2008; Clegg *et al.*, 1999). Thus, for comparison purposes, the N–CH₂ bonds in (II) are considered to adopt the *Nsp*²–CH₂ bond model, which does not exhibit anomeric effects. As shown in Table 1, the N2–C7 bond in (I) is much shorter than that for the model N–CH₂

bond. The N2–C7–N2ⁱ angle is also larger than the corresponding value found in a similar anomeric N–CH₂–N unit [112.6 (2)°; Zhang, Zhang *et al.*, 2009]. Therefore, as indicators of the anomeric effects, the nearly perpendicular/perpendicular conformation, the shortening of the N2–C7 bond and the opening of the N2–C7–N2ⁱ angle all point to the conclusion that there are two weak anomeric effects in the same C5–N2–C7–N2ⁱ–C5ⁱ unit, which are best rationalized in terms of *n*(N2) → σ^* (C7–N2ⁱ) stabilizing interactions. These findings constitute the first demonstration of two anomeric interactions in the same N–C–N fragment.

The supramolecular structure of (I) exhibits some interesting features. The molecules are linked into sheets by two different types of weak hydrogen bonds, one of the N–H···O type and one of the C–H···O type (Table 2). However, the structure can be relatively easily analyzed in terms of a simple one-dimensional chain. In analyzing the chain, for the sake of simplicity, we shall omit any consideration of intermolecular C–H···O interactions involving C4–H4 bonds from the aromatic rings (Table 2), which do not influence the overall supramolecular structure; thus, the chain involves only the N–H···O hydrogen bonds. Imine atom N2 at (*x, y, z*) acts as a hydrogen-bond donor to nitro atom O1 in the molecule at (*x, -y + 1, z + ½*), so generating by propagation along the *c*-glide plane at *y* = ½ a chain of molecules. This N–H···O interaction can be described by a graph-set motif of *C*(7) (Bernstein *et al.*, 1995). The twofold symmetry of the molecule means that there is a second series of identical N–H···O interactions running in the opposite direction along the chain of molecules. Thus, the molecules are actually linked into ladders, or chains of rings, where the rings formed by the two N–H···O interactions between pairs of adjacent molecules are centrosymmetric and can be described by the *R*₂²(18) motif. These rings are centered at (0, ½, *n*/2) (*n* = zero or integer; Fig. 2). The ladders are laterally linked into a sheet by one type of weak C–H···O hydrogen bond (Table 2). Benzene atom C6 in the molecule at (*x, y, z*) acts as a hydrogen-bonded donor to nitro atom O2 in the molecule at ($-x, -y + 2, -z$), so forming by inversion and the space-group symmetry a corrugated

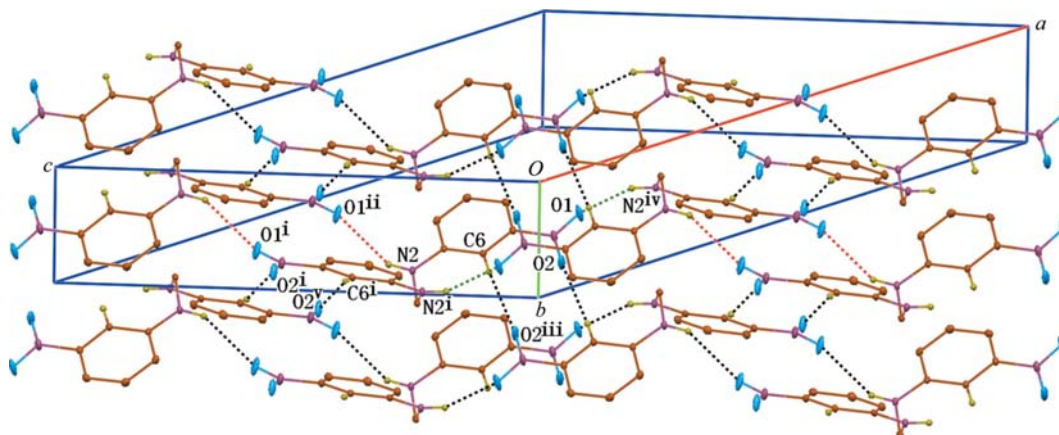


Figure 2

Part of the crystal structure of (I), showing the formation of a *C*(7) chain of *R*₂²(18) rings parallel to (001). For the sake of clarity, H atoms not involved in the motif shown have been omitted. Intermolecular interactions are represented by dashed lines. Selected atoms are labeled. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $-x, -y + 2, -z$; (iv) $x, -y + 1, z - \frac{1}{2}$; (v) $x, -y + 2, z + \frac{1}{2}$.]

hydrogen-bonded sheet parallel to (100) (Fig. 2). Two such sheets pass through each unit cell in the domains $\frac{1}{4} > x > -\frac{1}{4}$ and $\frac{3}{4} > x > \frac{1}{4}$, and there are no direction-specific interactions between adjacent sheets.

In conclusion, the crystal structure of (I) has permitted the demonstration for the first time of the existence of two anomeric effects in the C–N–C–N–C fragment, which are best rationalized in terms of $n(\text{N}) \rightarrow \sigma^*(\text{C–N})$ stabilizing interactions, and that the supramolecular structure exhibits a complex two-dimensional framework formed *via* two independent weak N–H...O and C–H...O hydrogen bonds.

Experimental

Into a three-necked round-bottomed flask equipped with a stirrer were introduced 3-nitroaniline (0.1 mol, 13.9 g), aqueous formaldehyde (0.05 mol, 37% 4.0 g) and ethanol (95%, 25 ml). The resulting mixture was refluxed with stirring for *ca* 10 min, and then the solution was cooled to room temperature. The precipitate was filtered off and washed with cool ethanol (95%). Crystals were obtained by slow cooling of a hot dimethylformamide solution of (I) to ambient temperature. ¹H NMR (dimethyl sulfoxide, 400 MHz): δ 7.45–7.07 (m, 8H), 7.16 (t, *J* = 5.6 Hz, 2H), 4.59 (t, *J* = 5.6 Hz, 2H).

Crystal data

| | |
|---|--------------------------------------|
| C ₁₃ H ₁₂ N ₄ O ₄ | <i>V</i> = 1270.7 (6) Å ³ |
| <i>M_r</i> = 288.36 | <i>Z</i> = 4 |
| Monoclinic, <i>C</i> 2/ <i>c</i> | Mo <i>K</i> α radiation |
| <i>a</i> = 24.517 (6) Å | <i>μ</i> = 0.12 mm ⁻¹ |
| <i>b</i> = 4.0505 (11) Å | <i>T</i> = 291 K |
| <i>c</i> = 16.222 (4) Å | 0.43 × 0.24 × 0.15 mm |
| <i>β</i> = 127.924 (2)° | |

Data collection

| | |
|--|--|
| Bruker SMART CCD diffractometer | 3715 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2003) | 1167 independent reflections |
| <i>T_{min}</i> = 0.890, <i>T_{max}</i> = 0.983 | 913 reflections with <i>I</i> > 2σ(<i>I</i>) |
| | <i>R_{int}</i> = 0.023 |

Refinement

| | |
|---------------------------------|--|
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | 96 parameters |
| $wR(F^2) = 0.148$ | H-atom parameters constrained |
| <i>S</i> = 1.04 | $\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{Å}^{-3}$ |
| 1167 reflections | $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$ |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------------------|------------|-----------------------|-----------|
| N2–C7 | 1.436 (2) | N2–C7–N2 ¹ | 115.6 (2) |
| C5–N2–C7–N2 ¹ | 81.18 (18) | | |

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

All H atoms were placed in idealized positions and allowed to ride on the respective parent atom, with C–H distances of 0.93 (aromatic) or 0.97 Å (CH₂) and an N–H distance of 0.86 Å, and with *U_{iso}*(H) values set at 1.2*U_{eq}*(C,N). The O atoms of the NO₂ groups have elongated atomic displacement ellipsoids, but a disorder model

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> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| N2–H2D...O1 ⁱⁱ | 0.86 | 2.57 | 3.354 (3) | 152 |
| C6–H6...O2 ⁱⁱⁱ | 0.93 | 2.59 | 3.499 (3) | 165 |
| C4–H4...O1 ⁱⁱ | 0.93 | 2.55 | 3.357 (3) | 145 |

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

was not employed because the ellipsoids of the disordered atoms remained elongated when such a model was considered.

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3134). Services for accessing these data are described at the back of the journal.

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