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Hydrogen-bonded chains in *N*-(2-nitrophenyl)phenylamine

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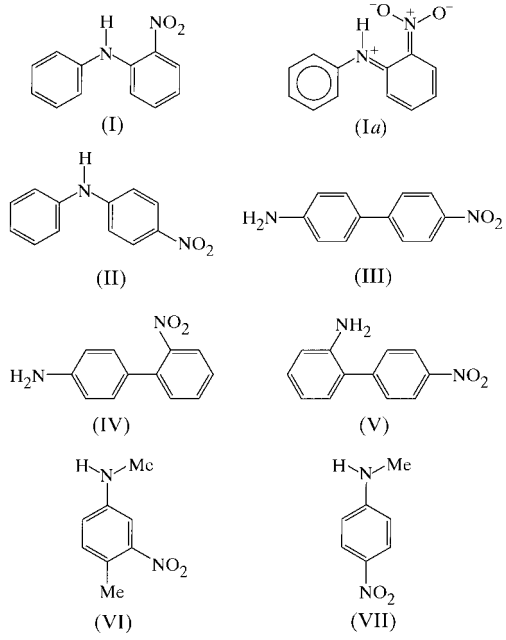
Molecules of the title compound, $C_{12}H_{10}N_2O_2$, are markedly non-planar. There is an intramolecular N—H···O hydrogen bond, and the molecules are linked into zigzag chains by a single C—H···O hydrogen bond. Comparisons are made with the supramolecular aggregation in isomeric amino–nitro derivatives, and in some *N*-methylnitroanilines.

Comment

The structures of C-methylated nitroanilines exhibit a wide range of supramolecular aggregation patterns (Cannon *et al.*, 2001; Ferguson *et al.*, 2001); in general, where there are no N-substituents, both N—H bonds and both N—O bonds participate in the hydrogen bonding. However, N-substitution necessarily produces a mismatch in the numbers of N—H and N—O bonds, opening the possibility of C—H···O hydrogen-bond formation wherever there is an excess of hard hydrogen-bond acceptors over hard hydrogen-bond donors. Here, we report the structure of such a nitroaniline, *N*-phenyl-2-nitroaniline [*N*-(2-nitrophenyl)phenylamine], (I).

Molecules of (I) exhibit a very wide C—N—C angle (Table 1), together with a conrotatory twist of the two independent aryl rings out of the central C—N—C plane. The wide angle is typical of sterically hindered secondary amines and the twisting of the rings, which is similar to that observed in Ph_3N (Sobolev *et al.*, 1985), may be ascribed to a compromise between minimization of repulsive H···H contacts between the rings and maximization of conjugative overlap between the rings and the imino N atom. The C—N distances are unusual: the two independent distances to N1 are not only significantly different, but they are both very long for their type, where the mean value is 1.353 Å (Allen *et al.*, 1987); the larger C—N—C—C torsion angles are associated with the longer C—N bond. The C—NO_2 distance is intermediate between the rather short bonds typically found in 2- and 4-nitroanilines, where electronic delocalization is possible, and the longer bonds found in unconjugated systems, such as 3-nitroanilines; at the same time, the nitro group is significantly twisted out of the plane of the adjacent aryl ring, so reducing the possible conjugation. While the C—C distances in the un-nitrated ring fall in a rather narrow range, those in the nitrated ring are consistent with a modest degree of conjugation, as in (I*a*).



In compound (I) (Fig. 1), there is an intramolecular N—H···O hydrogen bond, as typically found in 2-nitroanilines (Table 2). In addition, the molecules are weakly linked by C—H···O hydrogen bonds; C25 in the molecule at (*x*, *y*, *z*) acts as hydrogen-bond donor to O1 in the molecule at $(-\frac{1}{2}+x, 2-y, z)$, and propagation of this hydrogen bond produces a *C*(9) chain parallel to [100], generated by the glide plane at $y = 1.0$ (Fig. 2). There are two chains of this type running through each unit cell and they lie in the domains $-0.08 < z < 0.48$ and $0.42 < z < 0.98$; there are neither hydrogen bonds nor aromatic π–π-stacking interactions between the chains. It is striking that the same O atom, O1, is the acceptor of both hydrogen bonds in this structure (Table 2); despite the abundance of aromatic C—H bonds, O2 does not participate in the hydrogen bonding.

Despite repeated efforts to crystallize the isomeric 4-nitrodiphenylamine, (II), no crystals suitable for single-crystal X-ray analysis have been obtained. However, the structures

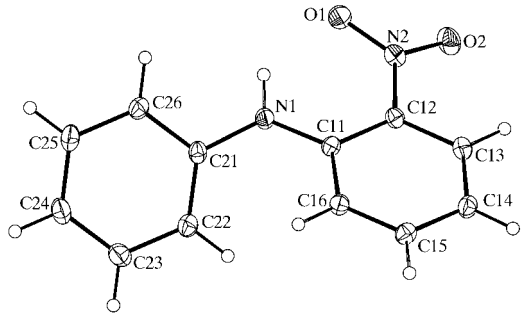


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

of three further isomeric aminonitrobiphenyls, (III)–(V), are available in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). In compound (III) (CSD code KEFLEM; Graham *et al.*, 1989), the amino group acts as a double donor and the nitro group as a double acceptor of N—H···O hydrogen bonds; each molecule is thereby linked to four others in a (4,4)-net (Batten & Robson, 1998) built from a single type of $R_4^4(30)$ ring, analogous to the (4,4)-net of $R_4^4(22)$ rings found in 4-nitroaniline itself (Tonogaki *et al.*, 1993). In the isomeric biphenyl (IV) (CSD code NIAMBP; Fallon & Ammon, 1974), the supramolecular structure is again two-dimensional. The amino group at (x, y, z) acts as donor, *via* H11, to both O atoms in the molecule at ($1 + x$, $-\frac{1}{2} - y$, $\frac{1}{2} + z$), so generating a $C(10)[R_1^2(4)]$ chain of rings parallel to [201]; the same amino group acts as donor, *via* H12, to O11 at (x, $-\frac{1}{2} - y$, $\frac{1}{2} + z$) producing a $C(10)$ chain parallel to [001]. The combination of the [201] and [001] chains generates a sheet structure (Fig. 3). Thus, while in both (III) and (IV), all the N—H and N—O bonds participate in the formation of hard hydrogen bonds, the pattern of these hydrogen bonds is entirely different. In (II), there is a simple pairing of N—H and N—O bonds, whereas in (IV), one N—H bond is linked to two O acceptors and one O acts as a double acceptor.

By contrast, in compound (V) (CSD code DIWFEU; Sutherland & Ali-Adib, 1986), one of the N—H bonds of the amino group plays no role in the hydrogen bonding, despite the numerical match between N—H and N—O bonds. The amino group at (x, y, z) acts, *via* a single H atom, as donor to both O atoms in the molecule at ($1 - x$, $-y$, $1 - z$). The resulting centrosymmetric dimer, centred at ($\frac{1}{2}$,0,$\frac{1}{2}$), thus contains two $R_1^2(4)$ rings and an $R_2^2(20)$ ring. Dimers of this type are linked into chains parallel to [1$\bar{1}$0]; atom C11 at (x, y, z) acts as hydrogen-bond donor to O2 at ($-\frac{1}{2} + x$, $\frac{1}{2} + y$, z) and propagation of this interaction yields a chain of fused alternating $R_2^2(20)$ and $R_4^2(12)$ rings (Fig. 4). Both O atoms in (V) participate in the hydrogen bonding, and the C—H···O hydrogen bond involves O2, which forms the longer of the two N—H···O hydrogen bonds in the $R_1^2(4)$ ring. Thus, the expected hydrogen-bonding role of one of the N—H bonds has apparently been usurped by a C—H bond.

Also in the CSD are the structures of the *N*-methyl derivatives (VI) (CSD code MNOMAN10; Chiaroni, 1971) and (VII) (CSD code FUXNAN; Panunto *et al.*, 1987). In (VI),

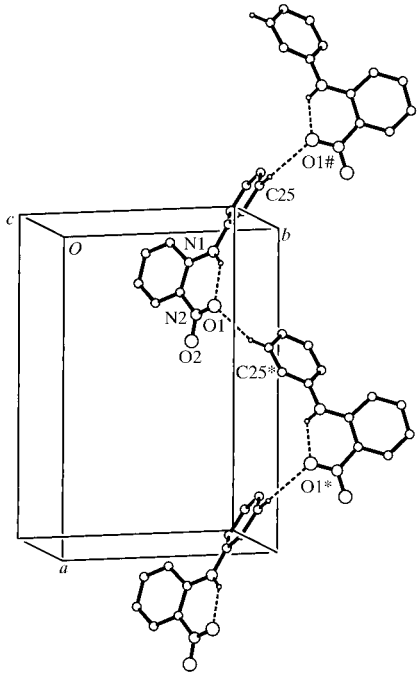


Figure 2
Part of the crystal structure of (II), showing the formation of a $C(9)$ zigzag chain. For the sake of clarity, H atoms not participating in the hydrogen bonding have been omitted. Atoms marked with an asterisk (*) or hash (#) are at the symmetry positions ($\frac{1}{2} + x$, $2 - y$, z) and ($-\frac{1}{2} + -x$, $2 - y$, z), respectively.

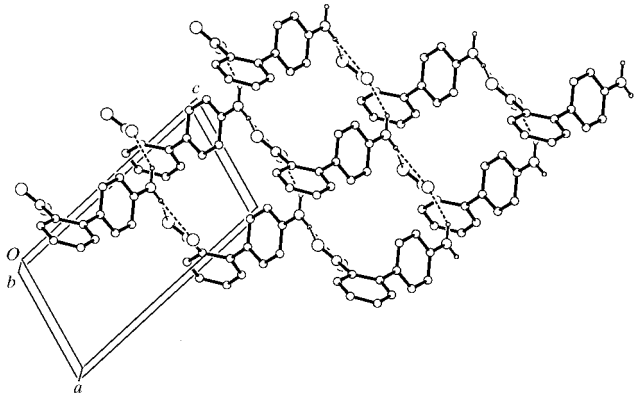


Figure 3
Part of the crystal structure of (IV) (Fallon & Ammon, 1974) showing the formation of a (010) sheet. For the sake of clarity, H atoms bonded to C atoms have been omitted.

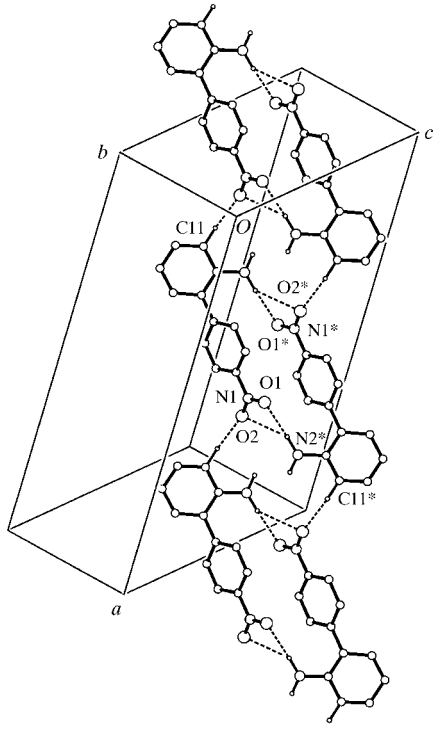


Figure 4
Part of the crystal structure of (V) (Sutherland & Ali-Adib, 1986), showing the formation of a chain of fused rings. For the sake of clarity, H atoms not participating in the hydrogen bonding have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($1 - x$, $-y$, $1 - z$).

there is a single N—H···O hydrogen bond linking the molecules into *C*(7) translational chains, while in (VII), the molecules are linked by a single N—H···O hydrogen bond into zigzag *C*(8) chains. In neither compound are there any aromatic C—H···O hydrogen bonds so that, as in compound (I), one of the O atoms plays no role in the hydrogen bonding.

Thus, even where there is a numerical match between the N—H and N—O bonds, not all of these are necessarily participants in the hydrogen bonding, as with compound (V). In compounds (I), (VI) and (VII), where there is an excess of hydrogen-bond acceptors, this does not necessarily lead to the formation of C—H···O hydrogen bonds.

Experimental

Crystals of (I) suitable for single-crystal X-ray diffraction were obtained by recrystallization from ethanol of a commercial sample, purchased from Aldrich. Two different commercial samples of (II) were purified by thin-layer chromatography. Attempts were made to obtain material suitable for single-crystal X-ray diffraction by crystallization from anhydrous ethanol, aqueous ethanol, chloroform and ethyl acetate, in all cases without success.

Crystal data

$C_{12}H_{10}N_2O_2$
M_r = 214.22
Orthorhombic, $Pca2_1$
a = 14.7077 (5) Å
b = 10.1602 (4) Å
c = 6.7878 (2) Å
V = 1014.32 (6) Å^3
Z = 4
D_x = 1.403 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1246 reflections
θ = 3.4–27.4°
μ = 0.10 mm^{-1}
T = 150 (2) K
Plate, orange
0.18 × 0.10 × 0.04 mm

Data collection

KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
T_{min} = 0.983, T_{max} = 0.996
9187 measured reflections
1246 independent reflections
1071 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 27.4°
$h = -18 \rightarrow 16$
$k = -13 \rightarrow 13$
$l = -7 \rightarrow 8$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.111
S = 1.08
1246 reflections
143 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0708P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.32 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.029 (7)

Compound (I) crystallized in the orthorhombic system. Space groups $Pca2_1$ and $Pcam$ were permitted by the systematic absences; the unit-cell volume indicated that Z = 4, and hence $Pca2_1$ was chosen, and confirmed by the successful structure analysis. H atoms were treated as riding atoms with distances C—H = 0.95 Å and N—H = 0.88 Å. In the absence of any significant anomalous scatterers, attempts to determine the absolute structure by Flack refinement (Flack, 1983) led to an inconclusive (Flack & Bernardinelli, 2000) value of the Flack parameter [1.1 (15)]; hence the Friedel equivalents were merged before the final refinements.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

Table 1
Selected geometric parameters (Å, °).

C11—C12	1.409 (3)	C21—C22	1.383 (3)
C12—C13	1.404 (3)	C22—C23	1.387 (2)
C13—C14	1.372 (3)	C23—C24	1.384 (4)
C14—C15	1.386 (3)	C24—C25	1.378 (5)
C15—C16	1.377 (3)	C25—C26	1.392 (3)
C16—C11	1.415 (3)	C26—C21	1.393 (4)
C12—N2	1.446 (3)	N1—C11	1.372 (3)
N2—O1	1.254 (3)	N1—C21	1.415 (3)
N2—O2	1.227 (2)		
C11—N1—C21	127.3 (2)		
C21—N1—C11—C12	162.4 (3)	C11—N1—C21—C22	−32.9 (4)
C21—N1—C11—C16	−19.5 (5)	C11—N1—C21—C26	150.9 (3)
C11—C12—N2—O1	15.7 (4)	C11—C12—N2—O2	−165.5 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.88	1.97	2.627 (3)	130
C25—H25···O1^{i}	0.95	2.56	3.219 (3)	127

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

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England, using an Enraf–Nonius KappaCCD diffractometer. The authors thank the staff for all their help and advice.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1481). Services for accessing these data are described at the back of the journal.

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