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2-Cyano-2′-nitrodiazoaminobenzene

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All atoms except for the two O atoms in the title compound, $C_{13}H_9N_5O_2$, are essentially coplanar as the nitro group is twisted by 12.0 (3)° with respect to its phenyl ring. The near planarity of the entire system is stabilized by an intramolecular hydrogen bond involving the nitro group which also limits the possible resonance forms of this molecule. The cyano group is slightly bent.

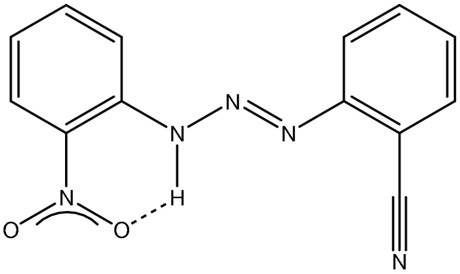
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.058
wR factor = 0.159
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structure of the title compound, (I), was undertaken to establish its structure as a precursor in the synthesis of a larger molecule. Specifically, a new route was sought to form a bond between an N and an aromatic C atom. Confirmation by X-ray analysis was deemed to be useful.



(I)

The rings in this molecule stack alternately *via* the inversion and translation along the a axis at interplanar distances which are consistent with π interactions; the distances correspond to the thickness (3.4 Å) of an aromatic ring (Pauling, 1960). The distance from the least-squares plane of the C7–C12 ring to the atoms in the C1–C6 ring (*via* inversion and translation of +1 in x) is 3.50 (3) Å; similarly, from the C1–C6 ring to C7–C12, 3.46 (3) Å.

The molecular skeleton is nearly planar as the maximum deviation from a least-squares plane involving all C and N atoms is 0.039 (3) Å for C12. The r.m.s. deviation for these fitted atoms is 0.020 Å. O1 lies 0.277 (4) Å above the plane; O2, 0.174 (4) Å below. The C2/N1/O1/O2 group has an r.m.s. deviation of 0.001 Å, while the plane of the nitro group is at an angle of 12.0 (3)° to the least-squares plane of the C1–C6 ring.

The cyano group is significantly (~8σ) bent [C8—C13—N5 = 176.7 (4)°]. This is likely due to intermolecular hydrogen bonds or dipole–dipole interactions (see Table 2) with O1, O2 and N5 and ring H atoms in adjoining molecules in the bc plane.

The intramolecular hydrogen bond between H2a and O2 (*cf.* Tables 1 and 2) restricts not only the rotation of the nitro group, but, as H2a is on N2, the probability of other resonance

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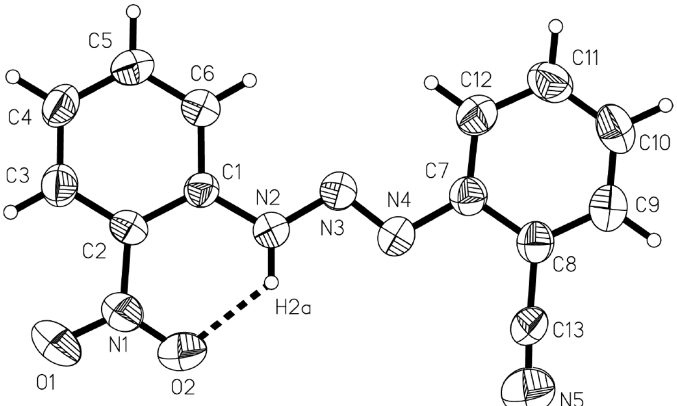

Figure 1
View of the title molecule showing the labeling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small spheres of arbitrary radii.

structures. It is likely that only the resonance structure shown in the Scheme makes a significant contribution, as is supported by the long N2—N3 bond length [1.337 (3) Å] and the short N3—N4 bond length [1.258 (3) Å]. N2—N3 is primarily a single bond; N3—N4, a double bond. To a lesser degree this is further corroborated by the O1—N1 bond length [1.220 (3) Å] being 5σ shorter than the O2—N1 bond [1.235 (3) Å], although this difference is not sufficient to prove that these bonds are localized double and single bonds, respectively. Presence of the intramolecular hydrogen bond is also supported by ^{1}H NMR, which shows a shift of 12.2 p.p.m. for H2a, indicating a high degree of deshielding. An additional consequence of the intramolecular hydrogen bond is that N1 is slightly off the center line from C5 to C2 [C5$\cdots$C2—N1 = 177.0 (2)°].

In both rings a pattern of C$\overset{\cdots}{-}$C bond length differences is consistent with the proximity of the three electron-withdrawing groups. The bonds involving C1 and C2 (C1—C2, C1—C6 and C2—C3) are significantly (>5σ) longer than those which are two bonds away from the groups involving N1 and N2 (*e.g.* C3—C4 and C5—C6). Similarly, bonds involving C7 and C8 (C7—C8, C7—C12 and C8—C9) are significantly (>5σ) longer than C9—C10, C10—C11 and C11—C12. In both rings the longest C$\overset{\cdots}{-}$C bond lengths are adjacent to a substituent, while the shortest lengths are two bonds away from the nearest substituent.

Experimental

Following a standard synthesis (Furniss *et al.*, 1989), the diazonium salt formed by the reaction of *m*-nitroaniline with sodium nitrite was allowed to react with anthranilonitrile (2-aminobenzonitrile). The bright yellow product formed was purified *via* chromatography (silica gel with chloroform as the eluent) and recrystallized by vapor diffusion of Et_2O into a $CHCl_3$ solution of the product. Analysis of the product by ^{1}H NMR was consistent with the formation of the desired C—N bond. MS data indicated that the mass of the title compound was 28 Daltons greater than what was originally expected, prior to the X-ray study, for a compound with but one N atom between the rings.

Crystal data

$C_{13}H_9N_5O_2$
$M_r = 267.25$
Triclinic, $P\overline{1}$
$a = 7.2080$ (10) Å
$b = 8.0106$ (12) Å
$c = 12.256$ (2) Å
$\alpha = 79.099$ (7)°
$\beta = 74.695$ (4)°
$\gamma = 69.379$ (6)°
$V = 635.2$ (2) Å^3
$Z = 2$
$D_x = 1.397$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 100 reflections
$\theta = 5.2$–12.5°
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Triangular plate, yellow
0.55 × 0.40 × 0.18 mm

Data collection

Siemens Bruker *P*4 diffractometer
$\theta/2\theta$ scans
2825 measured reflections
2247 independent reflections
1303 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.030$
$\theta_{\rm max} = 25.0°$
$h = -1 \rightarrow 8$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 14$
3 standard reflections every 100 reflections intensity decay: 2.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.159$
$S = 1.18$
2233 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2 + 0.1553P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.220 (3)	C3—C4	1.367 (4)
O2—N1	1.235 (3)	C4—C5	1.397 (4)
N1—C2	1.453 (4)	C5—C6	1.370 (4)
N2—N3	1.337 (3)	C7—C12	1.390 (4)
N2—C1	1.380 (4)	C7—C8	1.399 (4)
N3—N4	1.258 (3)	C8—C9	1.389 (4)
N4—C7	1.418 (4)	C8—C13	1.438 (5)
N5—C13	1.119 (4)	C9—C10	1.364 (5)
C1—C2	1.407 (4)	C10—C11	1.380 (5)
C1—C6	1.408 (4)	C11—C12	1.380 (4)
C2—C3	1.389 (4)		
O1—N1—O2	121.0 (3)	C3—C2—N1	117.1 (3)
O1—N1—C2	119.0 (3)	C1—C2—N1	121.5 (3)
O2—N1—C2	120.0 (3)	C12—C7—C8	118.6 (3)
N3—N2—C1	120.1 (2)	C12—C7—N4	125.0 (3)
N4—N3—N2	112.0 (2)	C5—C2—N1	177.0 (2)
N3—N4—C7	113.0 (2)	N5—C13—C8	176.7 (4)
N2—C1—C2	122.9 (3)	N1—O2—H2a	106
N2—C1—C6	120.2 (3)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2a$\cdots$O2	0.90	1.98	2.622 (3)	128
C5—H5$\cdots$O1$^{\rm i}$	0.96	2.90	3.468 (4)	119
C6—H6$\cdots$O1$^{\rm i}$	0.96	2.61	3.327 (4)	132
C9—H9$\cdots$N5$^{\rm ii}$	0.96	2.70	3.573 (5)	152
C10—H10$\cdots$N5$^{\rm i}$	0.96	2.62	3.473 (5)	148
C11—H11$\cdots$O2$^{\rm i}$	0.96	3.09	3.562 (5)	112
C12—H12$\cdots$O2$^{\rm i}$	0.96	2.58	3.308 (4)	133

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, -y, 1-z$.

Constrained bond lengths C—H 0.96 Å; N—H 0.90 Å. H2a was first located in a difference map, then placed into an ideal position. All other H's were placed in ideal positions (riding).

Data collection: *P*3/*P*4–*PC Diffractometer Program* (Siemens, 1991); cell refinement: *P*3/*P*4–*PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*90 (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXTL*/*PC* and *SHELXL*93.

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