p-Nitrophenyl isocyanide

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Achiral *p*-nitrophenyl isocyanide, $C_7H_4N_2O_2$, crystallizes in the orthorhombic chiral space group $P2_12_12_1$. Attractive intermolecular interactions between the nitro O atoms and both aromatic H and nitro N atoms of neighbouring molecules are observed. The $O \cdots N$ interaction is surprisingly strong [$N \cdots O = 2.869\ (2)$ Å] compared with other aromatic nitro compounds.

Comment

The title compound, *p*-nitroisocyanobenzene, (I), is achiral in solution but crystallizes in the orthorhombic chiral space group $P2_12_12_1$, with four symmetry-equivalent molecules in the unit cell. The bond lengths and angles of (I) are in the expected ranges for an aromatic isonitrile. The arene moiety is basically planar and the isocyano group, as well as the N atom of the nitro substituent, are located within 0.053 (3) Å of the mean plane of the benzene ring. The nitro group is rotated by 5.9 (2)° out of the benzene plane.


(I)
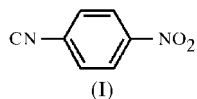
While the cyano isomer of (I), *p*-nitrobenzonitrile, is essentially isosteric with (I), it is not isostructural, and crystallizes in the space group $P2_1$ (Higashi & Osaki, 1977). In the Cambridge Structural Database (CSD, Version 5.25, November 2003 update; Allen, 2002), we found ten aromatic nitrile/isonitrile pairs. As with (I), the majority of these were not isostructural and, indeed, only four had at least one isomorphous nitrile/isonitrile pair.

In the case presented here, the formation of isomorphous crystals is prevented by surprisingly strong interactions of the nitro group with neighbouring molecules. Thus, each of the nitro O atoms is in close contact with either a neighbouring aromatic H atom or with the nitro N atom of a neighbouring molecule (Fig. 1). The $O1 \cdots H7^{ii}$ distance is 2.46 (2) Å and the corresponding $O1 \cdots C7^{ii}$ distance is 3.246 (2) Å [symmetry code: (ii) $x - 1$, $y + 1$, z]. While this $O \cdots H—C$ interaction is definitely attractive and stabilizing, it is in the usual range found for aromatic nitro compounds.

In sharp contrast, the $N—O \cdots N$ interaction of atom O2 with the neighbouring nitro group is surprisingly strong. Thus, the intermolecular distance between atoms O2 and $N2^i$ is 2.869 (2) Å [symmetry code: (i) $x + \frac{1}{2}, \frac{1}{2} - y, -z$]. Such a short intermolecular $N \cdots O$ distance is very rare for aromatic nitro compounds and only the extremely electron-poor superacid *N,N*-dipicrylamine, DPA, and some of its derivatives exhibit similarly short intermolecular $N \cdots O$ contacts (Woźniak *et al.*, 1994, 1997; Szumma *et al.*, 2000). Indeed, only the $N \cdots O$ distance of 2.826 Å observed for DPA itself is shorter than that observed for (I) (Woźniak *et al.*, 1994).

DPA has been analyzed in detail, both by a charge-density study (Platts *et al.*, 1995) and by computational methods using HNO_2 and FNO_2 as model compounds (Woźniak *et al.*, 2002). Both studies indicate that these types of bonds are mainly dispersive van der Waals-type interactions. Electrostatic stabilization seems to play only a minor role. The calculated $N \cdots O$ distance found by Platts *et al.* (1995). For HNO_2 lies between 2.8 and 2.9 Å, and both (I) and DPA fall well within this range. The strength of this interaction was estimated to be at least 10–13 kJ mol^{-1}, and is thus comparable with weak hydrogen-bond interactions.
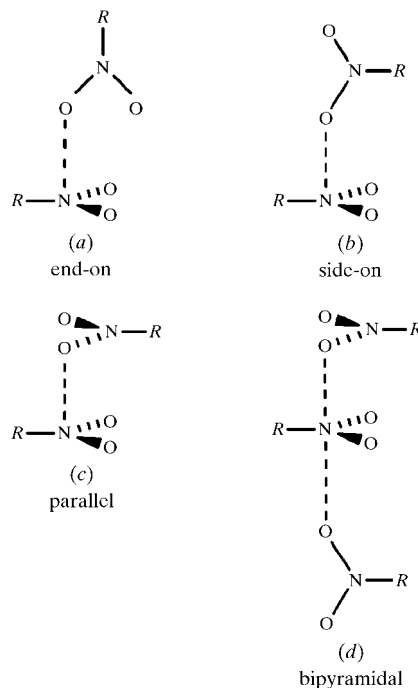

Based on these findings, short $N \cdots O$ contacts between nitro groups should be common among nitrobenzene derivatives, but the opposite is the case. For the bulk of organic nitro compounds, the average non-bonding distance between two nitro groups is around 3.3 Å and only a small fraction are shorter than the van der Waals radius of 3.07 Å (Szczesna & Urbańczyk-Lipkowska, 2002). Of all 5921 aromatic nitro compounds in the CSD, only *m*-chloronitrobenzene has an $N \cdots O$ distance shorter than 3.2 Å (Sharma *et al.*, 1985) (DPA and some of its derivatives are not listed in the CSD). This makes both (I) and DPA unusual cases, and a closer look at the geometry of the $N \cdots O$ interaction found in (I) seems appropriate.

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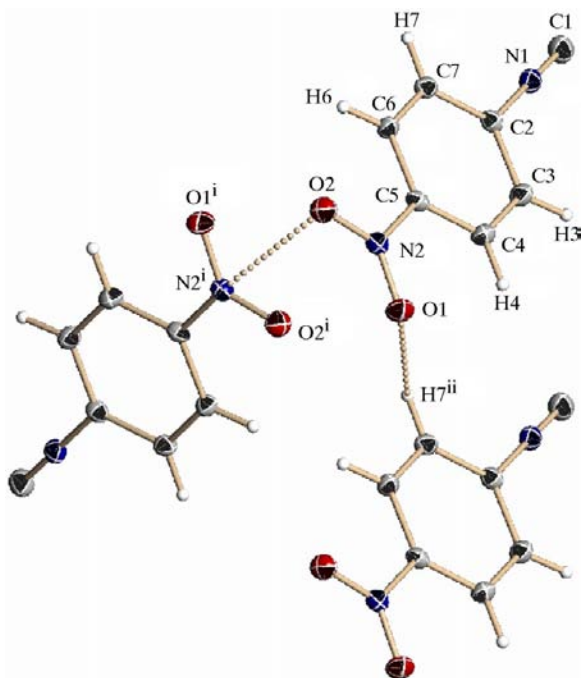
Figure 1
A plot of three molecules of (I), viewed along the *a* axis, showing the intermolecular O···N and O···H—C interactions. Displacement ellipsoids are drawn at the 30% probability level [symmetry codes: (i) $x + \frac{1}{2}$, $\frac{1}{2} - y$, $-z$; (ii) $x - 1$, $y + 1$, z].

As with hydrogen bonds, directionality is important for N···O interactions. The O atom in (I) is located directly atop the *p* orbital of the N atom of the neighbouring molecule, *i.e.* the line of the N···O interaction in (I) is perpendicular to the plane of the nitro group (Figs. 1 and 2).
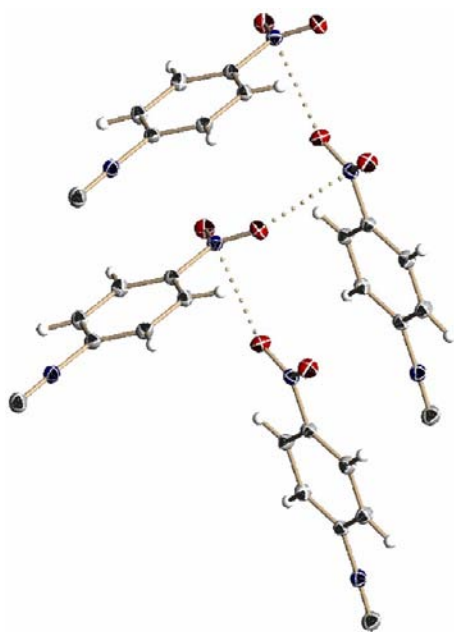
Figure 2
A diagram showing only the N···O intermolecular contacts in the structure of (I), viewed along the *b* axis. An infinite zigzag chain of molecules is formed by the N···O bridges.

The relative orientation of the O atom is not as important. For (I), an 'end-on coordination' of the O atom is observed and the direction of the O···N interaction is parallel to the C—N bond [(*a*) in the second scheme], resulting in the formation of an infinite zigzag chain of perpendicular molecules (Fig. 2). This end-on coordination was also found for DPA and some of its anions, but other alternative types of coordination, such as 'side-on', 'parallel' and bipyramidal are also observed [(*b*)–(*d*) in the second scheme] (Woźniak *et al.*, 1994).

The strengths of the N—O···H and N—O···N interactions found in (I) seem to be of the same order of magnitude, and neither of the two N—O bonds in the nitro group seems to be stabilized more than the other. The N—O bond lengths are 1.228 (2) and 1.226 (2) Å, respectively, and are thus basically identical.

Given the large structural difference between (I) and DPA, the fundamental reason for the anomalously short Ar–NO₂···Ar–NO₂ interactions which they share is not apparent. In particular, the relative poles of the electron-withdrawing groups on the arenes and the lattice effects remain unclear, and more detailed experimental and computational investigations will be necessary to explain the reasons for the observations made.

Experimental

The requisite intermediate, 1-formamido-4-nitrobenzene, was prepared by refluxing *p*-nitroaniline in 75% formic acid for 2 h. Addition of water precipitated the formamide, which was washed with water until neutral, dried *in vacuo* and recrystallized from hot acetone. The isocyanide, (I), was synthesized as described by Efraty *et al.* (1980) for 1,4-diisocyanobenzene, using two equivalents of diphosgene. It was purified by sublimation *in vacuo*. Single crystals of (I) were grown by sublimation *in vacuo*. Spectroscopic analysis, IR (toluene, CaF₂, ν, cm⁻¹): 2121 (*s*, isonitrile), 1520 (*s*, asymmetric NO₂), 1345 (*s*, symmetric NO₂); IR (KBr, ν, cm⁻¹): 2130 (*br*, isonitrile), 1541 (*br*, asymmetric NO₂), 1349 (*br*, symmetric NO₂); ¹H NMR (399.905 MHz, CDCl₃, δ): 8.23 [*d*, ³J(¹H¹H) = 9.0 Hz, 2H], 7.508 [*d*, ³J(¹H¹H) = 9.0 Hz, 2H]; ¹³C NMR (100.565 MHz, CDCl₃, δ): 169.3 (*s*, C isonitrile), 147.3 (*s*, C—NO₂), 131.0 [*t*, ¹J(¹³C¹⁴N) = 16 Hz, C—NC], 127.4 (*s*, C aromatic), 124.9 (*s*, C aromatic).

Crystal data

C₇H₄N₂O₂	Mo *K*α radiation
$M_r = 148.12$	Cell parameters from 6022
Orthorhombic, $P2_12_12_1$	reflections
$a = 5.0127$ (8) Å	$\theta = 3.4$–28.3°
$b = 6.0320$ (9) Å	$\mu = 0.11$ mm⁻¹
$c = 21.790$ (3) Å	$T = 90$ (2) K
$V = 658.86$ (18) Å³	Plate, colourless
$Z = 4$	$0.60 \times 0.29 \times 0.08$ mm
$D_x = 1.493$ Mg m⁻³	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	$R_{int} = 0.042$
	$\theta_{max} = 28.3°$
ω scans	$h = -6 \rightarrow 6$
6766 measured reflections	$k = -8 \rightarrow 7$
997 independent reflections	$l = -29 \rightarrow 29$
966 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2		$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2$	
$R(F) = 0.030$		$+ 0.6662P]$	
$wR(F^2) = 0.081$		where $P = (F_o^2 + 2F_c^2)/3$	
$S = 1.07$		$(\Delta/\sigma)_{max} < 0.001$	
997 reflections		$\Delta\rho_{max} = 0.29$ e Å^{-3}	
116 parameters		$\Delta\rho_{min} = -0.23$ e Å^{-3}	
All H-atom parameters refined			

Table 1
Selected geometric parameters (Å, °).

N2—O1	1.2259 (16)	N1—C1	1.155 (2)
N2—O2	1.2275 (16)	N1—C2	1.3999 (18)
N2—C5	1.4671 (18)		
O1—N2—O2	123.85 (13)	C4—C5—N2	118.64 (12)
O1—N2—C5	117.95 (12)	C6—C5—N2	118.48 (12)
O2—N2—C5	118.19 (11)	C7—C2—N1	119.38 (12)
C1—N1—C2	177.85 (16)	C3—C2—N1	118.48 (12)
O1—N2—C5—C4	−5.97 (18)	O1—N2—C5—C6	174.52 (12)
O2—N2—C5—C4	173.62 (12)	O2—N2—C5—C6	−5.90 (18)

Since compound (I) is achiral and does not contain heavy atoms, and since Mo radiation was used for the measurement, it was decided to omit refinement of chirality. Thus, despite (I) having a chiral space group, Friedel equivalents were merged. All H atoms were taken from a difference Fourier calculation and were refined isotropically.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL*2000 (Bruker, 2000); program(s) used to refine structure: *SHELXTL*2000; molecular graphics: *SHELXTL*2000; software used to prepare material for publication: *SHELXTL*2000.

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