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Isotypic crystal structures of 2,6-dibromo-*N*,*N*-bis(4-nitrophenyl)aniline and 2,6-dichloro-*N*,*N*-bis(4-nitrophenyl)aniline

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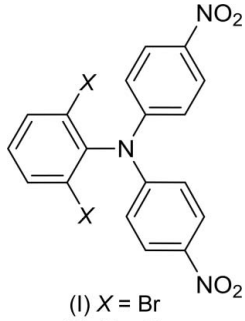
In the molecules of the two isotypic title compounds, $C_{18}H_{11}Br_2N_3O_4$ (I) and $C_{18}H_{11}Cl_2N_3O_4$ (II), the triphenylamine N atoms show no sign of pyramidalization, with marginal displacements of the N atoms from the mean plane of the three connecting C atoms: 0.0058 (13) Å for the Br compound (I) and 0.0074 (9) Å for the Cl compound (II). In the crystals, molecules are linked through C—H···O hydrogen bonds between phenyl rings and nitro groups and by *X*···O (*X* = Br, Cl) interactions, that are shorter than the sum of the van der Waals radii, leading to a three-dimensional network.

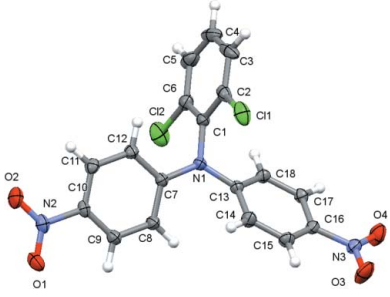
1. Chemical context

Arylamines are among the most important electron donors for functional organic materials, *e.g.* organic light emitting diodes (OLEDs) (Shirota & Kageyama, 2007; Tao *et al.*, 2011; Yook & Lee, 2012). In particular, triphenylamine-based compounds have received great attention due to their good hole-transport properties. Substituted triphenylamines are therefore highly desirable for further chemical modification, for example, cross-coupling or C—H activation.



(I) *X* = Br
(II) *X* = Cl

We have investigated the conversion of 2,6-dihalogenated anilines (*X* = Cl, Br) with 1-fluoro-4-nitrobenzene. Despite the sterical demand of the halogen substituents, no diphenylamine intermediates were obtained whereas the title tetra-substituted triphenylamines (I) and (II) could be isolated and their crystal structures are reported here.



2. Structural commentary

Representative for both structures, the molecular structure of compound (II) is displayed in Fig. 1. The isotypic relation of both structures is reflected in the nearly identical bond lengths and angles in the molecules of (I) and (II), and as expected, only the C—*X* distances (*X* = Br, Cl) differ significantly. The N

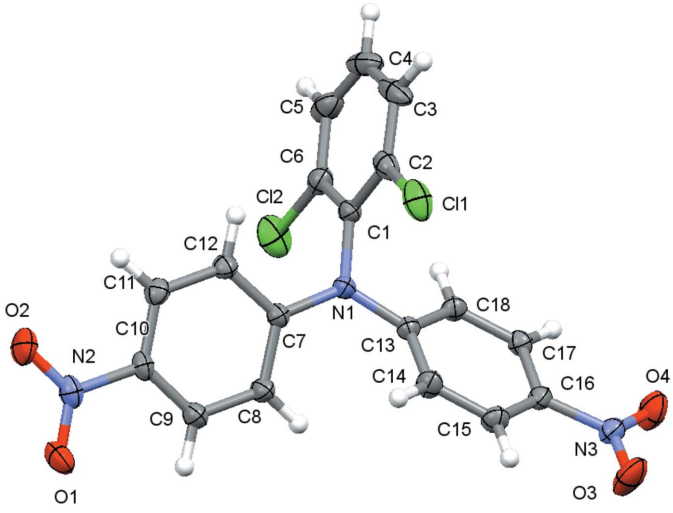


Figure 1
The molecular structure of compound (II), with atom labelling. Displacement ellipsoids are drawn at the 70% probability level.

atoms in both structures show no pyramidalization, with only marginal displacements from the planes of the bonded C atoms (C1/C7/C13) of 0.0058 (13) Å for (I) and of 0.0074 (9) Å for (II).

The dihedral angles between the benzene rings are 88.98 (7) (C1–C6)/(C13–C18), 82.07 (7) (C1–C6)/(C7–C12) and 51.97 (6)° (C7–C12)/(C13–C18) for (I). The corresponding values for (II) are 89.34 (4), 81.76 (5) and 49.41 (4)°.

The nitro groups are twisted slightly out of the plane of the benzene ring to which they are attached with dihedral angles of 8.29 (19) [(N3/O3/O4) / (C13–C18)] and 4.60 (19)° [(N2/O1/O2) / (C7–C11)] for (I). The corresponding values for (II) are 5.85 (13) and 4.81 (12)°.

3. Supramolecular features

The crystal packing of the structures of both (I) and (II) is consolidated by weak —C—H···O—N interactions (Tables 1 and 2) and *X*···O contacts that are shorter than the sum of the van der Waals radii (Bondi, 1964) of the respective elements. For (I) the Br···O contact is 3.3557 (13) Å, and for (II) the Cl···O contact is 3.2727 (9) Å. Both types of intermolecular interactions lead to the formation of a three-dimensional network (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, last update February 2014; Allen, 2002) indicated the presence of 759 molecules containing a triphenylamine backbone or of their metal-organic derivatives; they exclude, however, ring-closed systems such as *N*-phenylcarbazoles or *N*-phenylphenothiazines. None of these 759 molecules possesses the substitution pattern of the title compounds, *viz*. two *para*- and one *ortho*,*ortho*-substituted benzenes with respect to the N atom. The crystal structures of one *para*-nitro-substituted triphenylamine, *viz*. tris-(4-nitrophenyl)amine (Welch *et al.*, 2005) and one *ortho*,*ortho*-dichloro-substituted triphenylamine, *viz*. tris-(2,3,4,5,6-pentachlorophenyl)amine (Hayes *et al.*, 1980) have been reported. As in the title compounds, in both of these molecules the N atom is virtually coplanar with the three connecting C atoms. In the crystal structure of unsubstituted triphenylamine (Sobolev *et al.*, 1985), on the other hand, in three out of four molecules, the N atom is located distinctly out of the plane defined by the connecting C atoms.

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H1C5···O3^{i}	0.96	2.37	3.175 (2)	141
C12—H1C12···O2^{ii}	0.96	2.49	3.347 (2)	148

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

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H1C5···O3^{i}	0.96	2.35	3.1950 (15)	147
C12—H1C12···O2^{ii}	0.96	2.48	3.3304 (15)	148

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

5. Synthesis and crystallization

Compound (I) was prepared by heating 2,6-dichloroaniline (405 mg, 2.50 mmol, 1.0 eq.), 1-fluoro-4-nitrobenzene (353 mg, 2.50 mmol, 1.0 eq.) and Cs_2CO_3 (896 mg, 2.75 mmol, 1.1 eq.) in DMSO (5 ml) at 413 K for 26 h in a capped vial using a heating block. After cooling, the reaction mixture was poured into water and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Compound (I) was

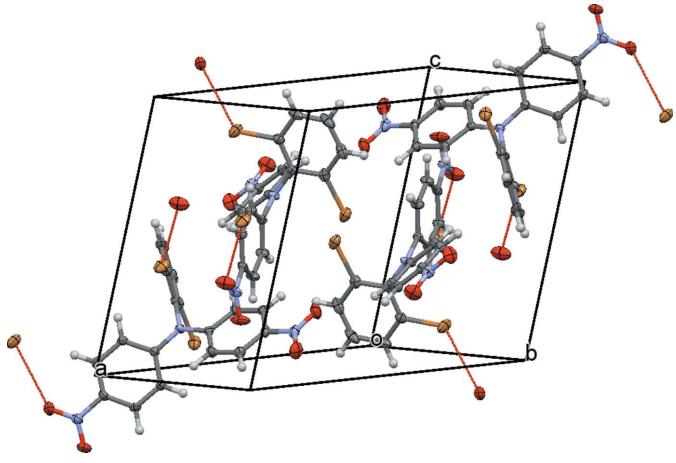


Figure 2
A view of the crystal packing of compound (I), sustained by Br···O van der Waals contacts [dashed lines; weak C—H···O interactions are also present but are not shown for clarity; colour code: O red, C grey, Br ochre, H white]. The displacement ellipsoids are drawn at the 70% probability level.

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{18}H_{11}Br_2N_3O_4$	$C_{18}H_{11}Cl_2N_3O_4$
M_r	493.1	404.2
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	13.4705 (7), 11.6686 (6), 11.7081 (7)	13.3117 (3), 11.5460 (3), 11.7558 (3)
β (°)	107.576 (2)	108.7971 (10)
V (Å^3)	1754.39 (17)	1710.46 (7)
Z	4	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	4.65	0.41
Crystal size (mm)	0.80 × 0.56 × 0.20	0.76 × 0.65 × 0.35
Data collection		
Diffractometer	Bruker *KAPPA* APEXII CCD	Bruker *KAPPA APEX*II CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.055, 0.390	0.74, 0.87
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	52187, 7731, 5557	29061, 4959, 4374
R_{int}	0.045	0.031
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.808	0.704
Refinement		
$R[F^2 > 3\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.079, 1.36	0.034, 0.131, 1.39
No. of reflections	7731	4959
No. of parameters	244	244
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.00, −0.91	0.24, −0.23

Computer programs: *APEX2* and *SAINT-Plus* (Bruker, 2013), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

obtained after column chromatography (light petroleum: EtOAc 7:3) as a yellow solid (374 mg, 0.93 mmol, 74%). Yellow single crystals were grown from a $CDCl_3$ solution by slow evaporation of the solvent. Spectroscopic data for compound (I) are available in the archived CIF.

Compound (II) was prepared by heating 2,6-dibromoaniline (627 mg, 2.50 mmol, 1.0 eq.), 1-fluoro-4-nitrobenzene (353 mg, 2.50 mmol, 1.0 eq.) and Cs_2CO_3 (896 mg, 2.75 mmol, 1.1 eq.) in DMSO (5 ml) at 413 K for 18 h in a capped vial using a heating block. After cooling, the reaction mixture was poured into water and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Compound (II) was obtained after crystallization from an EtOH/toluene mixture as a brown solid (237 mg, 0.48 mmol, 38%). Yellow single crystals were grown from a $CDCl_3$ solution by slow evaporation of the solvent. Spectroscopic data for compound (II) are available in the archived CIF.

6. Refinement

The hydrogen atoms in both structures, (I) and (II), were clearly discernible from difference Fourier maps and were refined as riding with C—H = 0.96 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. Experimental details are given in Table 3.

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Computing details

For both compounds, data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT-Plus* (Bruker, 2013); data reduction: *SAINT-Plus* (Bruker, 2013). Program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007) for (I); coordinates taken from Br analogue for (II). Program(s) used to refine structure: JANA2006 (Petříček, *et al.*, 2006) for (I); *JANA2006* (Petříček, *et al.*, 2006) for (II). For both compounds, molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(I) 2,6-Dibromo-*N*,*N*-bis(4-nitrophenyl)aniline

Crystal data

$C_{18}H_{11}Br_2N_3O_4$
M_r = 493.1
Monoclinic, $P2_1/c$
Hall symbol: -P 2ycb
a = 13.4705 (7) Å
b = 11.6686 (6) Å
c = 11.7081 (7) Å
β = 107.576 (2)°
V = 1754.39 (17) Å^3
Z = 4
$F(000)$ = 968
D_x = 1.866 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9998 reflections
θ = 2.9–34.9°
μ = 4.65 mm^{-1}
T = 100 K
Triangular prism, translucent yellow
0.80 × 0.56 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: X-ray tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.055, T_{max} = 0.390
52187 measured reflections
7731 independent reflections
5557 reflections with $I > 3\sigma(I)$
R_{int} = 0.045
θ_{max} = 35.1°, θ_{min} = 1.6°
h = −21→21
k = −18→18
l = −18→18

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.079
S = 1.36
7731 reflections
244 parameters
0 restraints
44 constraints
Primary atom site location: iterative
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0009I^2)$

$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 1.00 e Å^{-3}
$\Delta\rho_{min}$ = −0.91 e Å^{-3}

Special details

Experimental. Spectroscopic data for compound (**I**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.18 (d, J = 9.1 Hz, 4H), 7.56–7.49 (m, 2H), 7.40 (dd, J = 9.2, 6.6 Hz, 1H), 7.09 (d, J = 9.1 Hz, 4H) p.p.m.. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 149.3 (*s*), 143.0 (*s*), 138.0 (*s*), 136.4 (*s*), 130.6 (*d*), 130.1 (*d*), 125.6 (*d*), 120.4 (*d*) p.p.m..

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.573900 (13)	0.859367 (14)	0.064003 (15)	0.01908 (5)
Br2	0.901801 (14)	1.107097 (16)	0.387459 (16)	0.02362 (6)
O1	0.60098 (10)	1.55865 (11)	0.07605 (12)	0.0242 (4)
O2	0.52588 (11)	1.50312 (11)	0.20583 (12)	0.0258 (4)
O3	0.89116 (11)	0.84226 (12)	−0.27898 (11)	0.0275 (5)
O4	1.01356 (11)	0.77627 (12)	−0.12917 (12)	0.0279 (5)
N1	0.74647 (10)	1.04271 (11)	0.14278 (11)	0.0116 (4)
N2	0.57864 (11)	1.48465 (12)	0.13859 (12)	0.0169 (4)
N3	0.93586 (11)	0.83519 (12)	−0.17142 (12)	0.0166 (4)
C1	0.74189 (12)	0.96819 (13)	0.23780 (13)	0.0119 (4)
C2	0.67254 (13)	0.87583 (13)	0.21625 (15)	0.0146 (5)
C3	0.67200 (13)	0.79887 (15)	0.30661 (16)	0.0199 (5)
C4	0.73845 (14)	0.81727 (16)	0.42090 (16)	0.0225 (6)
C5	0.80581 (14)	0.90916 (15)	0.44579 (15)	0.0191 (5)
C6	0.80787 (13)	0.98333 (13)	0.35429 (14)	0.0150 (5)
C7	0.70196 (12)	1.15186 (12)	0.13580 (13)	0.0108 (4)
C8	0.72745 (13)	1.24028 (13)	0.06810 (14)	0.0143 (5)
C9	0.68543 (13)	1.34821 (13)	0.06712 (14)	0.0150 (5)
C10	0.61940 (12)	1.36934 (13)	0.13585 (14)	0.0132 (4)
C11	0.59367 (12)	1.28422 (13)	0.20434 (14)	0.0132 (4)
C12	0.63388 (12)	1.17542 (13)	0.20293 (13)	0.0128 (4)
C13	0.79772 (12)	0.99930 (12)	0.06341 (13)	0.0114 (4)
C14	0.75857 (13)	1.01765 (14)	−0.06029 (13)	0.0153 (5)
C15	0.80630 (13)	0.96656 (14)	−0.13642 (14)	0.0158 (5)
C16	0.89197 (12)	0.89691 (13)	−0.08923 (13)	0.0126 (4)
C17	0.93330 (12)	0.87926 (13)	0.03259 (14)	0.0138 (4)
C18	0.88567 (12)	0.93065 (13)	0.10882 (13)	0.0129 (4)
H1c3	0.62618	0.733863	0.289983	0.0239*
H1c4	0.737607	0.765079	0.483986	0.027*
H1c5	0.850818	0.921597	0.525706	0.023*
H1c8	0.774364	1.225481	0.02228	0.0171*
H1c9	0.701637	1.408126	0.019449	0.018*
H1c11	0.548604	1.300523	0.252057	0.0158*
H1c12	0.615028	1.115297	0.248386	0.0154*
H1c14	0.698685	1.065633	−0.092153	0.0183*
H1c15	0.780239	0.979303	−0.221267	0.0189*
H1c17	0.993928	0.83222	0.063785	0.0165*
H1c18	0.913367	0.918984	0.19371	0.0154*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01575 (8)	0.01677 (8)	0.02273 (9)	−0.00120 (6)	0.00282 (6)	−0.00462 (6)
Br2	0.02243 (9)	0.02083 (9)	0.02160 (9)	−0.00396 (7)	−0.00238 (7)	−0.00316 (7)
O1	0.0279 (7)	0.0125 (6)	0.0333 (7)	0.0028 (5)	0.0109 (6)	0.0051 (5)
O2	0.0296 (7)	0.0224 (6)	0.0294 (7)	0.0104 (5)	0.0153 (6)	−0.0009 (5)
O3	0.0331 (8)	0.0390 (8)	0.0116 (6)	0.0113 (6)	0.0086 (5)	0.0004 (5)
O4	0.0290 (7)	0.0353 (8)	0.0214 (6)	0.0179 (6)	0.0106 (6)	0.0037 (5)
N1	0.0163 (6)	0.0096 (5)	0.0106 (6)	0.0021 (4)	0.0063 (5)	0.0016 (4)
N2	0.0158 (6)	0.0131 (6)	0.0193 (7)	0.0025 (5)	0.0016 (5)	−0.0010 (5)
N3	0.0186 (7)	0.0181 (7)	0.0150 (6)	0.0022 (5)	0.0081 (5)	0.0015 (5)
C1	0.0141 (7)	0.0111 (6)	0.0125 (7)	0.0027 (5)	0.0069 (5)	0.0024 (5)
C2	0.0125 (7)	0.0127 (7)	0.0194 (8)	0.0026 (5)	0.0060 (6)	0.0010 (5)
C3	0.0153 (8)	0.0157 (7)	0.0320 (9)	0.0045 (6)	0.0120 (7)	0.0099 (7)
C4	0.0206 (8)	0.0251 (9)	0.0264 (9)	0.0105 (7)	0.0140 (7)	0.0151 (7)
C5	0.0201 (8)	0.0260 (9)	0.0132 (7)	0.0088 (6)	0.0077 (6)	0.0065 (6)
C6	0.0162 (7)	0.0154 (7)	0.0144 (7)	0.0017 (6)	0.0063 (6)	0.0004 (6)
C7	0.0121 (6)	0.0105 (6)	0.0099 (6)	0.0004 (5)	0.0034 (5)	0.0009 (5)
C8	0.0163 (7)	0.0132 (7)	0.0155 (7)	0.0010 (5)	0.0082 (6)	0.0020 (5)
C9	0.0167 (7)	0.0131 (7)	0.0165 (7)	0.0005 (5)	0.0068 (6)	0.0026 (5)
C10	0.0118 (7)	0.0112 (6)	0.0155 (7)	0.0017 (5)	0.0025 (5)	−0.0026 (5)
C11	0.0113 (7)	0.0146 (7)	0.0137 (7)	0.0003 (5)	0.0038 (5)	−0.0013 (5)
C12	0.0130 (7)	0.0127 (6)	0.0136 (7)	−0.0005 (5)	0.0054 (5)	0.0007 (5)
C13	0.0135 (7)	0.0101 (6)	0.0109 (6)	0.0003 (5)	0.0043 (5)	0.0002 (5)
C14	0.0162 (7)	0.0167 (7)	0.0124 (7)	0.0050 (6)	0.0036 (6)	0.0025 (5)
C15	0.0196 (8)	0.0180 (7)	0.0099 (6)	0.0037 (6)	0.0047 (6)	0.0030 (5)
C16	0.0141 (7)	0.0133 (7)	0.0123 (7)	0.0005 (5)	0.0067 (5)	−0.0007 (5)
C17	0.0140 (7)	0.0133 (7)	0.0135 (7)	0.0022 (5)	0.0033 (5)	0.0014 (5)
C18	0.0147 (7)	0.0138 (7)	0.0096 (6)	0.0010 (5)	0.0029 (5)	0.0010 (5)

Geometric parameters (Å, º)

Br1—N1	3.0882 (13)	C5—H1c5	0.96
Br1—C2	1.8840 (15)	C7—C8	1.405 (2)
Br2—N1	3.0869 (12)	C7—C12	1.403 (3)
Br2—C6	1.8817 (16)	C8—C9	1.379 (2)
O1—N2	1.227 (2)	C8—H1c8	0.96
O2—N2	1.228 (2)	C9—C10	1.390 (3)
O3—N3	1.2237 (17)	C9—H1c9	0.96
O4—N3	1.2247 (19)	C10—C11	1.385 (2)
N1—C1	1.428 (2)	C11—C12	1.382 (2)
N1—C7	1.3995 (19)	C11—H1c11	0.96
N1—C13	1.409 (2)	C12—H1c12	0.96
N2—C10	1.457 (2)	C13—C14	1.400 (2)
N3—C16	1.462 (2)	C13—C18	1.396 (2)
C1—C2	1.398 (2)	C14—C15	1.382 (3)
C1—C6	1.396 (2)	C14—H1c14	0.96

C2—C3	1.389 (3)	C15—C16	1.383 (2)
C3—C4	1.384 (2)	C15—H1c15	0.96
C3—H1c3	0.96	C16—C17	1.381 (2)
C4—C5	1.378 (3)	C17—C18	1.383 (3)
C4—H1c4	0.96	C17—H1c17	0.96
C5—C6	1.384 (2)	C18—H1c18	0.96

N1—Br1—C2	52.74 (6)	N1—C7—C8	121.85 (16)
N1—Br2—C6	52.88 (5)	N1—C7—C12	119.11 (14)
Br1—N1—Br2	133.15 (5)	C8—C7—C12	118.97 (14)
Br1—N1—C1	66.74 (7)	C7—C8—C9	120.36 (17)
Br1—N1—C7	110.03 (9)	C7—C8—H1c8	119.82
Br1—N1—C13	91.63 (8)	C9—C8—H1c8	119.82
Br2—N1—C1	66.54 (7)	C8—C9—C10	119.34 (16)
Br2—N1—C7	89.49 (8)	C8—C9—H1c9	120.33
Br2—N1—C13	111.71 (8)	C10—C9—H1c9	120.33
C1—N1—C7	118.76 (14)	N2—C10—C9	119.20 (15)
C1—N1—C13	116.10 (12)	N2—C10—C11	119.18 (16)
C7—N1—C13	125.13 (13)	C9—C10—C11	121.60 (15)
O1—N2—O2	123.55 (15)	C10—C11—C12	118.96 (16)
O1—N2—C10	118.34 (16)	C10—C11—H1c11	120.52
O2—N2—C10	118.09 (14)	C12—C11—H1c11	120.52
O3—N3—O4	123.27 (16)	C7—C12—C11	120.75 (15)
O3—N3—C16	118.22 (14)	C7—C12—H1c12	119.63
O4—N3—C16	118.47 (13)	C11—C12—H1c12	119.62
N1—C1—C2	120.82 (12)	N1—C13—C14	121.39 (13)
N1—C1—C6	121.30 (13)	N1—C13—C18	118.94 (13)
C2—C1—C6	117.86 (15)	C14—C13—C18	119.55 (16)
Br1—C2—C1	119.42 (12)	C13—C14—C15	119.86 (14)
Br1—C2—C3	119.35 (12)	C13—C14—H1c14	120.07
C1—C2—C3	121.17 (14)	C15—C14—H1c14	120.07
C2—C3—C4	119.04 (16)	C14—C15—C16	119.38 (14)
C2—C3—H1c3	120.48	C14—C15—H1c15	120.31
C4—C3—H1c3	120.48	C16—C15—H1c15	120.31
C3—C4—C5	121.18 (17)	N3—C16—C15	118.75 (13)
C3—C4—H1c4	119.41	N3—C16—C17	119.29 (14)
C5—C4—H1c4	119.41	C15—C16—C17	121.85 (16)
C4—C5—C6	119.27 (14)	C16—C17—C18	118.74 (14)
C4—C5—H1c5	120.37	C16—C17—H1c17	120.63
C6—C5—H1c5	120.37	C18—C17—H1c17	120.63
Br2—C6—C1	119.26 (12)	C13—C18—C17	120.58 (14)
Br2—C6—C5	119.31 (11)	C13—C18—H1c18	119.71
C1—C6—C5	121.42 (15)	C17—C18—H1c18	119.71

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H1C5···O3^{i}	0.96	2.37	3.175 (2)	141

C12—H1C12···O2^{ii}	0.96	2.49	3.347 (2)	148

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1/2.

(II) 2,6-Dichloro-*N*,*N*-bis(4-nitrophenyl)aniline

Crystal data

$C_{18}H_{11}Cl_2N_3O_4$
M_r = 404.2
Monoclinic, $P2_1/c$
Hall symbol: -P 2ycb
a = 13.3117 (3) Å
b = 11.5460 (3) Å
c = 11.7558 (3) Å
β = 108.7971 (10)°
V = 1710.46 (7) Å^3
Z = 4
$F(000)$ = 824
D_x = 1.569 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9690 reflections
θ = 3.9–30.0°
μ = 0.41 mm^{-1}
T = 100 K
Block, translucent yellow
0.76 × 0.65 × 0.35 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: X-ray tube
Graphite monochromator
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.74, T_{max} = 0.87
29061 measured reflections
4959 independent reflections
4374 reflections with $I > 3\sigma(I)$
R_{int} = 0.031
θ_{max} = 30.0°, θ_{min} = 1.6°
h = −18→18
k = −16→15
l = −16→16

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.131
S = 1.39
4959 reflections
244 parameters
0 restraints
44 constraints
Primary atom site location: isomorphous structure methods
Hydrogen site location: isomorphous structure methods
H-atom parameters constrained
Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0064I^2)$
$(\Delta/\sigma)_{max}$ = 0.018
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Special details

Experimental. Spectroscopic data for compound (**II**): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.19 (d, J =9.2 Hz, 4H), 7.74 (d, J = 8.1 Hz, 2H), 7.25 (t, J = 8.1 Hz, 1H), 7.10 (d, J = 9.2 Hz, 4H) p.p.m.. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 144.9 (*s*), 142.9 (*s*), 140.6 (*s*), 134.1 (*d*), 131.5 (*d*), 126.5 (*s*), 125.5 (*d*), 120.5 (*d*) p.p.m..

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.58310 (2)	0.86376 (2)	0.06717 (3)	0.02676 (11)
Cl2	0.89794 (2)	1.09658 (2)	0.39011 (3)	0.02968 (11)
O1	0.59995 (7)	1.56656 (7)	0.07725 (8)	0.0250 (3)
O2	0.52501 (8)	1.50838 (7)	0.20576 (9)	0.0278 (3)
O3	0.90032 (8)	0.85088 (9)	−0.27494 (8)	0.0324 (3)
O4	1.01290 (8)	0.76623 (8)	−0.12423 (8)	0.0288 (3)

N1	0.75055 (7)	1.04563 (7)	0.14397 (7)	0.0145 (3)
N2	0.57820 (7)	1.49072 (7)	0.13910 (8)	0.0183 (3)
N3	0.94009 (7)	0.83429 (8)	−0.16642 (8)	0.0174 (3)
C1	0.74413 (8)	0.96904 (8)	0.23650 (9)	0.0145 (3)
C2	0.67230 (9)	0.87665 (8)	0.21010 (10)	0.0185 (3)
C3	0.66959 (9)	0.79754 (9)	0.29820 (12)	0.0260 (4)
C4	0.73555 (11)	0.81422 (10)	0.41472 (12)	0.0297 (4)
C5	0.80543 (10)	0.90616 (10)	0.44433 (11)	0.0253 (4)
C6	0.80964 (9)	0.98244 (9)	0.35460 (10)	0.0184 (3)
C7	0.70496 (8)	1.15578 (8)	0.13637 (9)	0.0133 (3)
C8	0.73029 (9)	1.24530 (8)	0.06960 (9)	0.0166 (3)
C9	0.68665 (9)	1.35445 (8)	0.06821 (10)	0.0172 (3)
C10	0.61973 (8)	1.37467 (8)	0.13544 (9)	0.0151 (3)
C11	0.59475 (8)	1.28778 (8)	0.20337 (9)	0.0158 (3)
C12	0.63582 (8)	1.17818 (8)	0.20218 (9)	0.0151 (3)
C13	0.80210 (8)	1.00128 (8)	0.06577 (9)	0.0137 (3)
C14	0.76400 (9)	1.02286 (8)	−0.05822 (9)	0.0179 (3)
C15	0.81196 (9)	0.97117 (8)	−0.13329 (9)	0.0174 (3)
C16	0.89655 (8)	0.89650 (8)	−0.08506 (9)	0.0141 (3)
C17	0.93636 (8)	0.87409 (8)	0.03712 (9)	0.0145 (3)
C18	0.88927 (8)	0.92743 (8)	0.11260 (9)	0.0146 (3)
H1c3	0.622526	0.732212	0.27836	0.0311*
H1c4	0.732728	0.760843	0.476226	0.0357*
H1c5	0.850452	0.917238	0.525723	0.0303*
H1c8	0.777925	1.230913	0.024835	0.02*
H1c9	0.702539	1.415466	0.021211	0.0206*
H1c11	0.549454	1.3037	0.250608	0.019*
H1c12	0.616983	1.116869	0.246644	0.0181*
H1c14	0.704527	1.073604	−0.090899	0.0215*
H1c15	0.786988	0.986778	−0.218011	0.0209*
H1c17	0.995418	0.822599	0.06882	0.0174*
H1c18	0.91652	0.913735	0.197601	0.0175*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01996 (17)	0.02079 (16)	0.0347 (2)	−0.00131 (9)	0.00215 (13)	−0.00737 (10)
Cl2	0.02831 (18)	0.02495 (16)	0.02653 (18)	−0.00245 (10)	−0.00402 (13)	−0.00497 (10)
O1	0.0279 (4)	0.0138 (3)	0.0335 (5)	0.0024 (3)	0.0100 (4)	0.0026 (3)
O2	0.0302 (5)	0.0245 (4)	0.0330 (5)	0.0096 (3)	0.0163 (4)	−0.0016 (3)
O3	0.0390 (5)	0.0457 (5)	0.0141 (4)	0.0168 (4)	0.0108 (4)	0.0031 (3)
O4	0.0294 (5)	0.0346 (4)	0.0233 (4)	0.0162 (4)	0.0100 (4)	0.0014 (3)
N1	0.0186 (4)	0.0124 (3)	0.0139 (4)	0.0030 (3)	0.0073 (3)	0.0024 (3)
N2	0.0166 (4)	0.0150 (4)	0.0212 (4)	0.0035 (3)	0.0031 (3)	−0.0018 (3)
N3	0.0181 (4)	0.0198 (4)	0.0160 (4)	0.0011 (3)	0.0078 (3)	0.0000 (3)
C1	0.0167 (5)	0.0128 (4)	0.0158 (5)	0.0029 (3)	0.0076 (4)	0.0025 (3)
C2	0.0161 (5)	0.0135 (4)	0.0277 (6)	0.0025 (3)	0.0093 (4)	0.0016 (4)
C3	0.0205 (5)	0.0164 (4)	0.0473 (8)	0.0057 (4)	0.0198 (5)	0.0120 (4)

C4	0.0322 (6)	0.0284 (5)	0.0390 (7)	0.0167 (5)	0.0260 (6)	0.0208 (5)
C5	0.0297 (6)	0.0309 (5)	0.0179 (5)	0.0146 (5)	0.0114 (5)	0.0087 (4)
C6	0.0205 (5)	0.0195 (4)	0.0156 (5)	0.0042 (4)	0.0064 (4)	0.0005 (4)
C7	0.0134 (4)	0.0121 (4)	0.0139 (4)	0.0009 (3)	0.0040 (3)	0.0004 (3)
C8	0.0187 (5)	0.0151 (4)	0.0192 (5)	0.0030 (3)	0.0103 (4)	0.0030 (3)
C9	0.0198 (5)	0.0135 (4)	0.0193 (5)	0.0022 (3)	0.0078 (4)	0.0027 (3)
C10	0.0139 (5)	0.0125 (4)	0.0181 (5)	0.0020 (3)	0.0039 (4)	−0.0015 (3)
C11	0.0133 (4)	0.0174 (4)	0.0176 (5)	0.0006 (3)	0.0061 (4)	−0.0010 (3)
C12	0.0145 (4)	0.0147 (4)	0.0171 (5)	−0.0002 (3)	0.0067 (4)	0.0008 (3)
C13	0.0155 (5)	0.0123 (4)	0.0133 (4)	0.0005 (3)	0.0048 (4)	−0.0001 (3)
C14	0.0200 (5)	0.0187 (4)	0.0144 (5)	0.0060 (4)	0.0045 (4)	0.0026 (3)
C15	0.0199 (5)	0.0192 (4)	0.0131 (4)	0.0035 (4)	0.0051 (4)	0.0026 (3)
C16	0.0151 (4)	0.0142 (4)	0.0144 (4)	−0.0003 (3)	0.0067 (4)	−0.0009 (3)
C17	0.0138 (4)	0.0140 (4)	0.0148 (4)	0.0013 (3)	0.0033 (4)	0.0005 (3)
C18	0.0160 (5)	0.0152 (4)	0.0114 (4)	0.0013 (3)	0.0030 (4)	0.0009 (3)

Geometric parameters (Å, º)

Cl1—N1	2.9827 (9)	C7—C8	1.4032 (15)
Cl2—N1	2.9848 (8)	C7—C12	1.4041 (17)
O1—N2	1.2308 (13)	C8—C9	1.3855 (14)
O2—N2	1.2307 (16)	C8—H1c8	0.96
O3—N3	1.2285 (12)	C9—C10	1.3880 (18)
O4—N3	1.2219 (12)	C9—H1c9	0.96
N1—C1	1.4256 (14)	C10—C11	1.3878 (15)
N1—C7	1.3996 (12)	C11—C12	1.3803 (14)
N1—C13	1.4087 (15)	C11—H1c11	0.96
N2—C10	1.4553 (13)	C12—H1c12	0.96
N3—C16	1.4573 (15)	C13—C14	1.4027 (14)
C1—C2	1.3991 (14)	C13—C18	1.4017 (13)
C1—C6	1.3898 (13)	C14—C15	1.3805 (17)
C2—C3	1.3901 (18)	C14—H1c14	0.96
C3—C4	1.3818 (17)	C15—C16	1.3861 (14)
C3—H1c3	0.96	C15—H1c15	0.96
C4—C5	1.3801 (17)	C16—C17	1.3858 (14)
C4—H1c4	0.96	C17—C18	1.3850 (16)
C5—C6	1.3891 (17)	C17—H1c17	0.96
C5—H1c5	0.96	C18—H1c18	0.96
Cl1—N1—Cl2	128.74 (3)	C7—C8—C9	120.08 (11)
Cl1—N1—C1	64.63 (5)	C7—C8—H1c8	119.96
Cl1—N1—C7	110.73 (6)	C9—C8—H1c8	119.96
Cl1—N1—C13	91.15 (5)	C8—C9—C10	119.33 (10)
Cl2—N1—C1	64.21 (4)	C8—C9—H1c9	120.33
Cl2—N1—C7	91.08 (5)	C10—C9—H1c9	120.33
Cl2—N1—C13	113.45 (6)	N2—C10—C9	119.43 (9)
C1—N1—C7	118.75 (9)	N2—C10—C11	119.00 (11)
C1—N1—C13	115.72 (8)	C9—C10—C11	121.52 (9)

C7—N1—C13	125.53 (9)	C10—C11—C12	119.20 (11)
O1—N2—O2	123.46 (9)	C10—C11—H1c11	120.4
O1—N2—C10	118.27 (10)	C12—C11—H1c11	120.4
O2—N2—C10	118.25 (9)	C7—C12—C11	120.43 (10)
O3—N3—O4	122.81 (11)	C7—C12—H1c12	119.78
O3—N3—C16	118.37 (9)	C11—C12—H1c12	119.78
O4—N3—C16	118.80 (9)	N1—C13—C14	121.63 (9)
N1—C1—C2	120.56 (8)	N1—C13—C18	118.72 (9)
N1—C1—C6	121.37 (9)	C14—C13—C18	119.51 (10)
C2—C1—C6	118.06 (10)	C13—C14—C15	120.04 (9)
C1—C2—C3	121.05 (9)	C13—C14—H1c14	119.98
C2—C3—C4	119.09 (10)	C15—C14—H1c14	119.98
C2—C3—H1c3	120.45	C14—C15—C16	119.31 (9)
C4—C3—H1c3	120.45	C14—C15—H1c15	120.34
C3—C4—C5	121.24 (12)	C16—C15—H1c15	120.34
C3—C4—H1c4	119.38	N3—C16—C15	118.73 (9)
C5—C4—H1c4	119.38	N3—C16—C17	119.22 (8)
C4—C5—C6	119.01 (10)	C15—C16—C17	121.94 (11)
C4—C5—H1c5	120.49	C16—C17—C18	118.70 (9)
C6—C5—H1c5	120.49	C16—C17—H1c17	120.65
C1—C6—C5	121.48 (10)	C18—C17—H1c17	120.65
N1—C7—C8	121.84 (10)	C13—C18—C17	120.48 (9)
N1—C7—C12	118.69 (9)	C13—C18—H1c18	119.76
C8—C7—C12	119.40 (9)	C17—C18—H1c18	119.76

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H1C5···O3^{i}	0.96	2.35	3.1950 (15)	147
C12—H1C12···O2^{ii}	0.96	2.48	3.3304 (15)	148

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) −*x*+1, *y*−1/2, −*z*+1/2.