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A series of *N*-(2-phenylethyl)nitroaniline derivatives as precursors for slow and sustained nitric oxide release agents

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2,4-Dinitro-*N*-(2-phenylethyl)aniline, $C_{14}H_{13}N_3O_4$, (I), crystallizes with one independent molecule in the asymmetric unit. The adjacent amine and nitro groups form an intramolecular N—H···O hydrogen bond. The *anti* conformation about the ethyl C—C bond leads to the phenyl and aniline rings being essentially parallel. Molecules are linked into dimers by intermolecular N—H···O hydrogen bonds, such that each amine H atom participates in a three-centre interaction with two nitro O atoms. Though the dimers pack so that the arene rings of adjacent molecules are parallel, the rings are staggered and π–π interactions do not appear to be favoured. 4,6-Dinitro-*N*,*N*′-bis(2-phenylethyl)benzene-1,3-diamine, $C_{22}H_{22}N_4O_4$, (II), differs from (I) in the presence of a second 2-phenylethylamine group on the substituted ring. Compound (II) also crystallizes with one unique molecule in the asymmetric unit. Both amine groups are involved in intramolecular N—H···O hydrogen bonds with adjacent nitro groups. Although one ethyl group adopts an *anti* conformation as in (I), the other is *gauche*, with the result that the pendant phenyl rings are not parallel. The amine group that is part of the *gauche* conformation participates in a three-centre N—H···O hydrogen bond with the nitro group of a neighbouring molecule, leading to dimers as in (I). The other amine H atom does not form any intermolecular hydrogen bonds. The packing leads to separations of *ca* 3.4 Å of the parallel *anti* phenyl and aminobenzene rings. 2-Cyano-4-nitro-*N*-(2-phenylethyl)aniline, $C_{15}H_{13}N_3O_2$, (III), differs from (I) only in having a cyano group in place of the 2-nitro group. The absence of the adjacent nitro group eliminates the intramolecular N—H···O hydrogen bond. Molecules of (III) adopt the same *anti* conformation about the ethyl group as in (I), but crystallize in the higher-symmetry monoclinic space group $P2_1/n$. The molecules are linked into dimers *via* N—H···N amine–cyano hydrogen bonds, while the nitro groups are not involved in any N—H···O interactions. Owing to the different symmetry, the molecules pack in a herringbone pattern with fewer face-to-face interactions between the rings. The closest such interactions are about 3.5 Å between rings that are largely slipped past one another. 4-Methylsulfonyl-2-nitro-*N*-(2-phenylethyl)aniline, $C_{15}H_{16}N_2O_4S$, (IV), differs from (I) in having a methylsulfonyl group in place of the 4-nitro group. The intramolecular N—H···O hydrogen bond is present as in (I). However, unlike (I), the conformation about the ethyl group is *gauche*, so the two arene rings are nearly perpendicular rather than parallel. The packing is significantly different from the other three structures in that there are no intermolecular hydrogen bonds involving the N—H groups. The molecules are arranged in tetragonal columns running along the *c* axis, with the aniline rings mostly parallel and separated by *ca* 3.7 Å. Taken together, these structures demonstrate that modest changes in functional groups cause significant differences in molecular conformation, intermolecular interactions and packing.

Keywords: crystal structure; *N*-(2-phenylethyl)nitroaniline derivatives; secondary amines; nitric oxide release agents.

1. Introduction

Nitric oxide (NO) is known for its significance as a messenger molecule in essentially every organ system across many life forms: mammals, plants, fish and insects (Giles, 2006). In humans, NO has important functions in the cardiovascular, nervous, respiratory and immune systems. It plays vital roles in protecting the heart, brain and kidneys. NO activities within these systems include facilitating endothelium-dependent vasodilation; regulating blood pressure, vascular tone and compliance; and inhibiting platelet aggregation, vascular inflammatory factors, leukocyte adhesion and smooth muscle cell proliferation (Mason & Cockcroft, 2006). Metabolic activity, sexual response, insulin release and the peripheral nervous system are affected by NO as well (Giles, 2006).

Numerous factors (including aging, hypercholesterolaemia, smoking and diabetes mellitus) can contribute to the loss of NO bioavailability and/or lack of NO production, resulting in endothelial dysfunction (Cai *et al.*, 2005). Diseases and disorders based on NO malfunction include hypertension, atherosclerosis, cardiovascular disease, asthma, pulmonary hypertension, erectile dysfunction, preeclampsia and insulin resistance (Giles, 2006).

In order to ameliorate deleterious conditions arising out of NO shortfall, numerous NO donors have been developed, most of which release NO in a single high-concentration burst (Cai *et al.*, 2005). We have reported a series of *N*-nitrosated secondary amines which release NO in a slow, sustained and rate-tunable manner (Wang *et al.*, 2009; Yu *et al.*, 2011; Curtis *et al.*, 2013). Furthermore, the released NO has been shown to inhibit the proliferation of human aortic smooth muscle cells, a contributing factor to the progression of atherosclerosis (Yu *et al.*, 2011; Curtis *et al.*, 2013). As part of this continuing study, we report herein the syntheses and X-ray crystal structures of four secondary amines that are precursors to slow and

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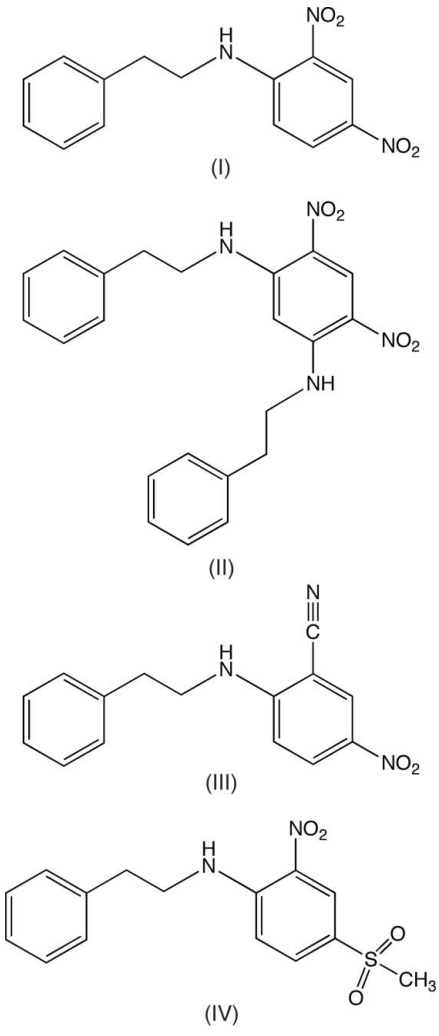
sustained NO-releasing agents. These secondary amines, 2,4-dinitro-*N*-(2-phenylethyl)aniline, (I), 4,6-dinitro-*N*,*N*′-bis(2-phenylethyl)benzene-1,3-diamine, (II), 2-cyano-4-nitro-*N*-(2-phenylethyl)aniline, (III), and 4-methylsulfonyl-2-nitro-*N*-(2-phenylethyl)aniline, (IV), were prepared by the reactions of 2-phenylethylamine and four different activated aromatic mono- and difluorides, namely 2,4-dinitrofluorobenzene for (I), 1,5-difluoro-2,4-dinitrobenzene for (II), 2-cyano-4-nitrofluorobenzene for (III) and (3-nitro-4-fluorophenyl)methyl sulfone for (IV).



2. Experimental

2.1. Synthesis and crystallization

For the synthesis of 2,4-dinitro-*N*-(2-phenylethyl)aniline, (I), a 100 ml three-necked round-bottomed flask, equipped with a magnetic stirrer bar, nitrogen inlet, air condenser and thermometer, was charged with 2-phenylethylamine (PEA; 0.6370 g, 5.26 mmol), 2,4-dinitrofluorobenzene (0.9775 g, 5.25 mmol), potassium carbonate (1.4489 g, 10.48 mmol) and dimethylacetamide (DMAC, 50 ml). The vials used to weigh PEA and 2,4-dinitrofluorobenzene were washed with DMAC (5 ml) and the washes were transferred to the reaction vessel. The reaction vessel was heated using an oil bath until the temperature of the reaction mixture reached 343 K. The reaction was allowed to proceed with stirring for 12 h, after which the DMAC was removed by distillation at reduced pressure. The crude product was dissolved in dichloromethane (75 ml) and washed with a saturated sodium chloride solution (200 ml), followed by two washes with deionized water (200 ml). The organic layer was separated and anhydrous magnesium sulfate was added to dry the product. The resulting mixture was filtered and the filtrate was evaporated at reduced pressure using a rotary evaporator. Crystals of (I) suitable for X-ray diffraction were obtained by recrystallization from a dichloromethane–hexane solution (4:1 *v*/*v*) (yield 69%; m.p. 425–427 K). Spectroscopic analysis for (I): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.8 (overlapping peaks, 2H), 8.2 (*dd*, J_1 = 10.00, J_2 = 3.33 Hz, 1H), 7.3–7.2 (overlapping peaks, 6H), 3.7 (*q*, J = 6.36 Hz, 2H), 2.9 (*t*, J = 7.58 Hz, 2H); IR (NaCl, ν, cm^{-1}): 3361, 3124, 3070, 3036, 2969, 2938, 2860, 1622, 1592, 1550, 1525, 1501, 1452, 1418, 1380, 1337, 1313.

Compounds (II)–(IV) were prepared in a similar manner, using 1,5-difluoro-2,4-dinitrobenzene for (II) (yield 62%; m.p. 408–409 K), 2-cyano-4-nitrofluorobenzene for (III) (yield 73%; m.p. 427–429 K) and (3-nitro-4-fluorophenyl)methyl sulfone for (IV) (yield 63%; m.p. 414–416 K) in place of 2,4-dinitrofluorobenzene. Spectroscopic analysis for (II): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.9 (*s*, 1H), 8.4 (*t*, J = 5.45 Hz, 2H), 7.3–7.2 (overlapping peaks, 10H), 5.8 (*s*, 1H), 3.6 (*q*, J = 6.97 Hz, 4H), 3.0 (*t*, J = 7.27 Hz, 4H); IR (NaCl, ν, cm^{-1}): 3360, 1617, 1540, 1474, 1456, 1348, 1308. Spectroscopic analysis for (III): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.4 (*d*, J = 3.33 Hz, 1H), 8.1 (*dd*, J_1 = 9.70, J_2 = 2.73 Hz, 1H), 7.6 (*t*, J = 5.76 Hz, 1H), 7.3–7.2 (overlapping peaks, 5H), 6.9 (*d*, J = 9.39 Hz, 1H), 3.5 (*q*, J = 6.36 Hz, 2H), 2.9 (*t*, J = 7.58 Hz, 2H); IR (NaCl, ν, cm^{-1}): 3353, 2222, 1610, 1587, 1541, 1507, 1497, 1456, 1337, 1321. Spectroscopic analysis for (IV): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.6 (*t*, J = 5.78 Hz, 1H), 8.5 (*d*, J = 2.42 Hz, 1H), 7.9 (*dd*, J_1 = 7.58, J_2 = 2.12 Hz, 1H), 7.3–7.2 (overlapping peaks, 6H), 3.7 (*q*, J = 5.78 Hz, 2H), 3.2 (*s*, 3H), 2.9 (*t*, J = 7.58 Hz, 2H); IR (NaCl, ν, cm^{-1}): 3369, 3088, 3063, 3023, 2927, 2869, 1616, 1569, 1521, 1466, 1456, 1431, 1411, 1359, 1307.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located from difference Fourier syntheses and refined isotropically without any restraints [N—H = 0.866 (15)–0.900 (17) Å and C—H = 0.898 (13)–1.006 (16) Å].

3. Results and discussion

2,4-Dinitro-*N*-(2-phenylethyl)aniline, (I), crystallizes in the triclinic space group $P\overline{1}$ with one independent molecule in the asymmetric unit (Fig. 1). As we (Payne *et al.*, 2010) and others (Panunto *et al.*, 1987; Clegg *et al.*, 1994) have observed previously, the adjacent amine and nitro groups form an intramolecular N—H···O hydrogen bond (Table 2). The ethyl group adopts an *anti* conformation [N1—C7—C8—C9 =

Table 1
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$C_{14}H_{13}N_3O_4$	$C_{22}H_{22}N_4O_4$	$C_{15}H_{13}N_3O_2$	$C_{15}H_{16}N_2O_4S$
M_r	287.27	406.44	267.28	320.36
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/n$	Tetragonal, $I4_1/a$
Temperature (K)	100	100	100	100
a, b, c (Å)	7.235 (2), 7.282 (2), 13.512 (4)	8.1121 (7), 10.1819 (8), 13.1018 (11)	7.4871 (5), 16.270 (1), 10.8432 (7)	20.4639 (13), 20.4639 (13), 14.3952 (14)
α, β, γ (°)	88.714 (5), 85.131 (5), 67.239 (5)	93.466 (1), 106.595 (1), 106.932 (1)	90, 94.384 (1), 90	90, 90, 90
V (Å^3)	654.0 (4)	979.88 (14)	1317.00 (15)	6028.3 (10)
Z	2	2	4	16
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.11	0.10	0.09	0.24
Crystal size (mm)	0.20 × 0.10 × 0.02	0.20 × 0.10 × 0.05	0.40 × 0.20 × 0.10	0.40 × 0.20 × 0.20
Data collection				
Diffractometer	Bruker APEX DUO CCD area-detector diffractometer	Bruker APEX DUO CCD area-detector diffractometer	Bruker APEX DUO CCD area-detector diffractometer	Bruker APEX DUO CCD area-detector diffractometer
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.978, 0.998	0.981, 0.995	0.964, 0.991	0.912, 0.955
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9039, 3158, 2288	17364, 6868, 5289	23007, 4732, 4189	52424, 5524, 5155
R_{int}	0.027	0.018	0.018	0.018
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.661	0.767	0.765	0.765
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.104, 1.03	0.043, 0.121, 1.03	0.038, 0.113, 1.04	0.029, 0.086, 1.06
No. of reflections	3158	6868	4732	5524
No. of parameters	242	359	233	263
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.29, −0.26	0.57, −0.21	0.56, −0.20	0.51, −0.31

Computer programs: *APEX2* (Bruker, 2005), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *CrystalMaker* (Palmer, 2013).

−173.75 (12)°], with the result that the phenyl and aniline rings are nearly parallel. This is the same overall molecular conformation that was observed in the related compound *N*-[2-(2-formylphenyl)ethyl]-2-nitroaniline (Clegg *et al.*, 1994).

Neighbouring molecules of (I) are linked into dimers across centres of inversion by an intermolecular N—H···O hydrogen bond between the amine group of one molecule and the nitro group of the other (Fig. 2). The amine H1 atom thus participates in a three-centre hydrogen bond with two nitro O21 atoms, and each O21 atom serves as an acceptor for both intra- and intermolecular hydrogen bonds (Table 2). The intermolecular H1···O21^{i} distance of 2.381 (19) Å [symmetry code: (i) $-x+1, -y, -z+1$] is within the typical range for this type of N—H···O amine–nitro interaction (Panunto *et al.*, 1987). The absence of a more extended hydrogen-bond network (*i.e.* chains) is a departure from what we had found in an earlier study of a related set of arenes with similar functional groups (Payne *et al.*, 2010). Owing to the triclinic symmetry of (I), all of the arene rings in the crystal structure are parallel to one another and they are approximately parallel to the (110) plane. Although the plane-to-plane distance (*ca* 3.4 Å) is short enough for π–π interactions, the rings are staggered rather than face-to-face, suggesting that such interactions are not important in this structure.

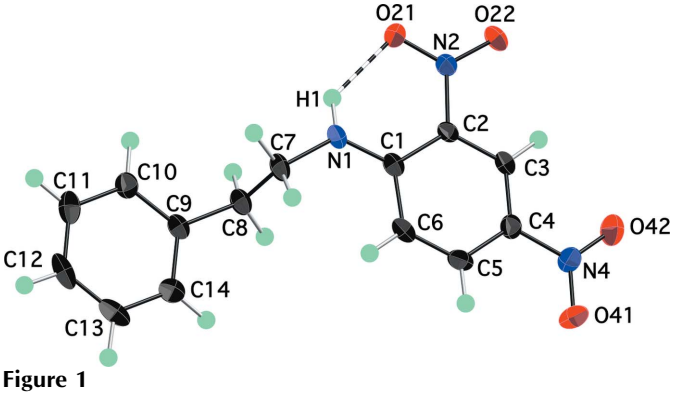


Figure 1
The molecular structure of (I), showing atom labels and 70% probability displacement ellipsoids for non-H atoms. The intramolecular hydrogen bond is shown as a dashed line.

4,6-Dinitro-*N*,*N*′-bis(2-phenylethyl)benzene-1,3-diamine, (II), differs from (I) only in having a second 2-phenylethylamine group in the 5-position on the nitro ring. As in (I), both amine H atoms form intramolecular N—H···O hydrogen

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21	0.867 (19)	1.983 (19)	2.6377 (16)	131.5 (16)
N1—H1···O21^{i}	0.867 (19)	2.381 (19)	3.0823 (18)	138.3 (16)

Symmetry code: (i) $-x+1, -y, -z+1$.

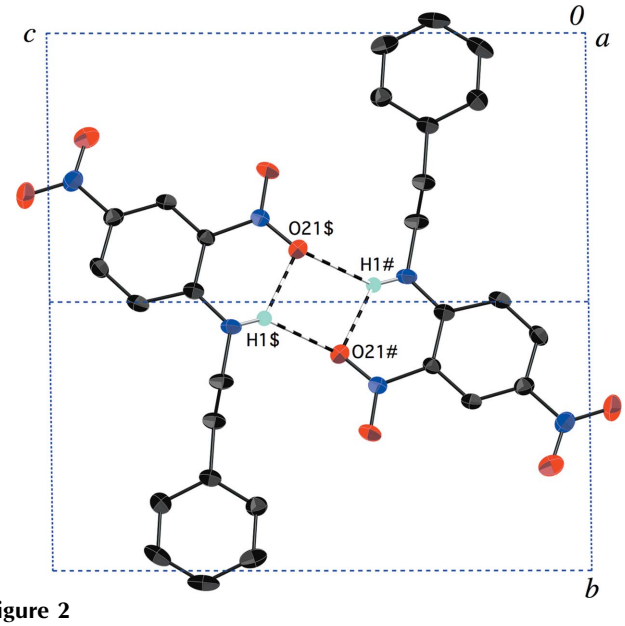


Figure 2
Molecules of (I) are linked into dimers across centres of inversion by N—H···O amine–nitro hydrogen bonds (dashed lines). The view is onto the (100) plane. [Symmetry codes: (#) $x, y+1, z$; ($) $-x+1, -y+1, -z+1$.]

bonds with the adjacent nitro groups (Table 3). Although the two halves of the molecule through the central ring are chemically identical, in the crystal structure the molecule possesses no internal symmetry (Fig. 3) because the two 2-phenylethyl groups adopt different conformations. One, as in (I), is *anti* [N1—C7—C8—C9 = 172.60 (8)°], while the other is *gauche* [N5—C15—C16—C17 = −66.94 (10)°]. As a result, the C1–C6 and C9–C14 rings are nearly parallel, but the C17–C22 ring is approximately orthogonal to the other rings.

The packing of (II) has features in common with that of (I). Compound (II) also crystallizes in the $P\overline{1}$ space group with one independent molecule in the asymmetric unit, and the molecules are linked into dimers across centres of inversion *via* three-centre N—H···O amine–nitro hydrogen bonds (Fig. 4 and Table 3). The intermolecular H5···O41^{i} distance of 2.800 (17) Å in (II) [symmetry code: (i) $-x+2, -y+2, -z+1$] is significantly longer than that in (I), but it is still in the observed range for a second amine–nitro contact (Panunto *et al.*, 1987). Although there are two amine groups in (II), only that involving the *gauche* 2-phenylethyl group participates in intermolecular hydrogen bonds. Therefore, as was the case in (I), there are no hydrogen-bonded chains in (II). The molecules pack with the nitro and *anti*-phenyl rings approximately parallel to $(\overline{1}10)$. Neighbouring rings are *ca* 3.5 Å apart and overlap more than in (I), suggesting greater π–π interaction.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21	0.891 (15)	1.935 (15)	2.6318 (11)	133.8 (13)
N5—H5···O41	0.900 (17)	1.967 (16)	2.6358 (11)	129.8 (14)
N5—H5···O41^{i}	0.900 (17)	2.800 (17)	3.5877 (11)	146.8 (13)

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

2-Cyano-4-nitro-*N*-(2-phenylethyl)aniline, (III), differs from (I) only in having a cyano group in place of the 2-nitro group. Since the 2-nitro group adjacent to the amine is absent, there is no intramolecular hydrogen bond in (III). The molecule adopts the same *anti* conformation seen in (I) [N1—C7—C8—C9 = −171.53 (6)°] (Fig. 5). Molecules of (III) are linked into dimers across centres of inversion by N—H···N amine–cyano hydrogen bonds (Fig. 6 and Table 4). The nitro groups are not involved in any hydrogen bonds. A similar amine–cyano dimerization was observed in 2,6-bis(ethylamino)-3-nitrobenzonitrile (Payne *et al.*, 2010), though in that case the molecules were also joined by three-centre N—H···O amine–nitro hydrogen bonds involving the other amine group. In

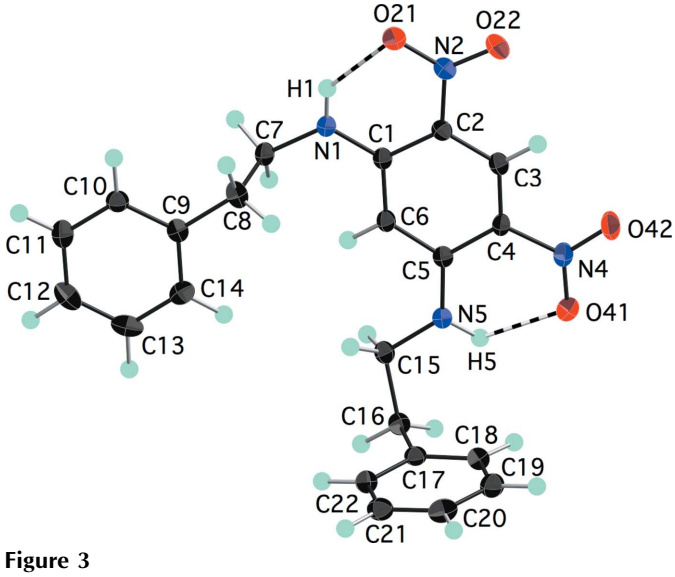


Figure 3
The molecular structure of (II), showing atom labels and 70% probability displacement ellipsoids for non-H atoms. Intramolecular hydrogen bonds are shown as dashed lines.

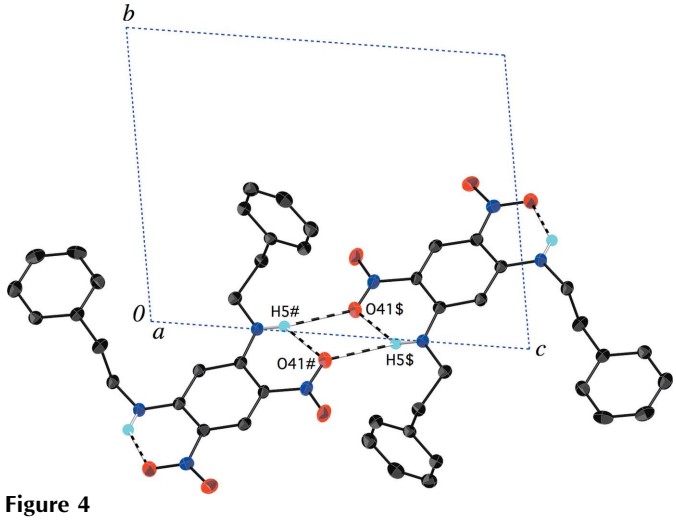


Figure 4
Molecules of (II) are linked into dimers across centres of inversion by weak N—H···O amine–nitro hydrogen bonds (dashed lines). The view is onto the (100) plane. [Symmetry codes: (#) $x, y-1, z$; ($) $-x+2, -y+1, -z+1$.]

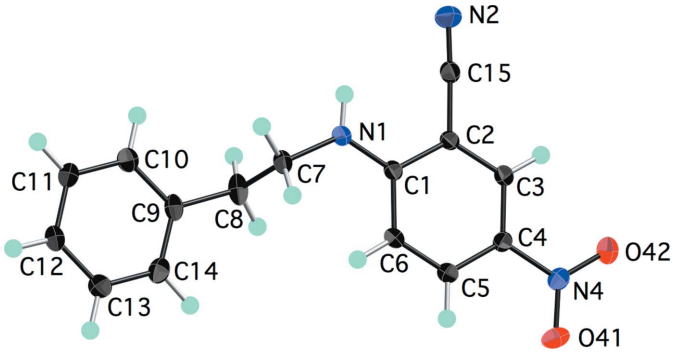


Figure 5
The molecular structure of (III), showing atom labels and 70% probability displacement ellipsoids for non-H atoms.

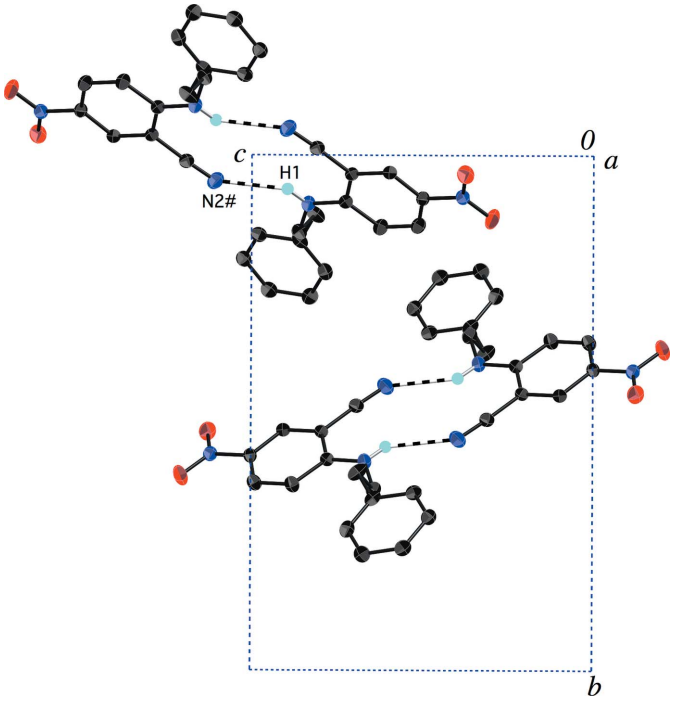


Figure 6
Molecules of (III) are linked into dimers across centres of inversion by N—H···N hydrogen bonds (dashed lines) between the amine H and cyano N atom. [Symmetry code: (#) $-x+1, -y, -z+2$.]

(III), the single amine H atom is not available for additional interactions.

The packing in (III) shows some notable differences from that seen in (I). The compound crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$), which does not require all of the rings to be oriented in the same direction. Instead, we see more of a herringbone pattern (Fig. 6) in which most of the

Table 4
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···N2^{i}	0.866 (15)	2.300 (15)	3.0287 (10)	141.9 (12)

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

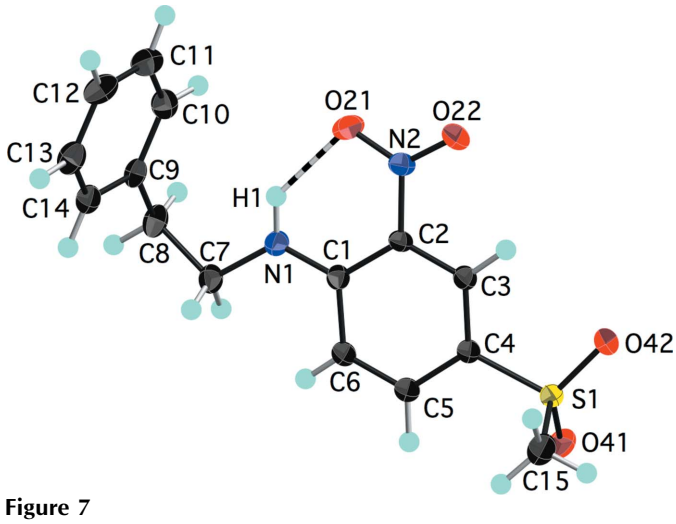


Figure 7
The molecular structure of (IV), showing atom labels and 70% probability displacement ellipsoids for non-H atoms. The intramolecular hydrogen bond is shown as a dashed line.

nearby arene rings are not parallel to each other. The closest contacts between the aniline rings (*ca* 3.4 Å) involve rings that are mostly slipped past each other. In this, *i.e.* the apparent lack of strong π–π interactions, the structure of (III) is consistent with (I) and (II).

4-Methylsulfonyl-2-nitro-*N*-(2-phenylethyl)aniline, (IV), is modified from (I) in having a methylsulfonyl group in place of the 4-nitro group. The amine and 2-nitro groups form the expected intramolecular hydrogen bond but, unlike (I) and (III), the 2-phenylethyl group adopts a *gauche* conformation [N1—C7—C8—C9 = −61.20 (8)°] (Fig. 7). Such an arrangement was also observed in a 2,4-dinitroaniline derivative in which the 2-phenylethyl group is functionalized at the α-ethyl C atom (Williams *et al.*, 2011). Unlike the other compounds studied here, there are no intermolecular hydrogen bonds of any significance in the structure of (IV). The closest H···O contact, H1···O22($-y+\frac{5}{4}, x-\frac{1}{4}, z-\frac{1}{4}$) [3.26 (2) Å], is well beyond a reasonable H···A distance for a normal two-centre hydrogen bond. The absence of amine–sulfone interactions is surprising, as such hydrogen bonds have been shown to be favoured in similar systems (Glidewell *et al.*, 2001; Glidewell & Ferguson, 1996; Bertolasi *et al.*, 1993).

In addition to the lack of intermolecular hydrogen bonding, the crystal packing in (IV) is substantially different from that in (I)–(III). First, the compound crystallizes in the tetragonal system, space group $I4_1/a$ ($Z = 16$). According to a previous study of over 29000 organic compounds (Mighell *et al.*, 1983), only *ca* 2.9% are tetragonal. Of the 68 tetragonal space groups, $I4_1/a$ is the second most popular among organic compounds, with over 11% of the occurrences being in that system.

Table 5
Hydrogen-bond geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O21	0.882 (16)	1.951 (16)	2.6364 (9)	133.4 (14)

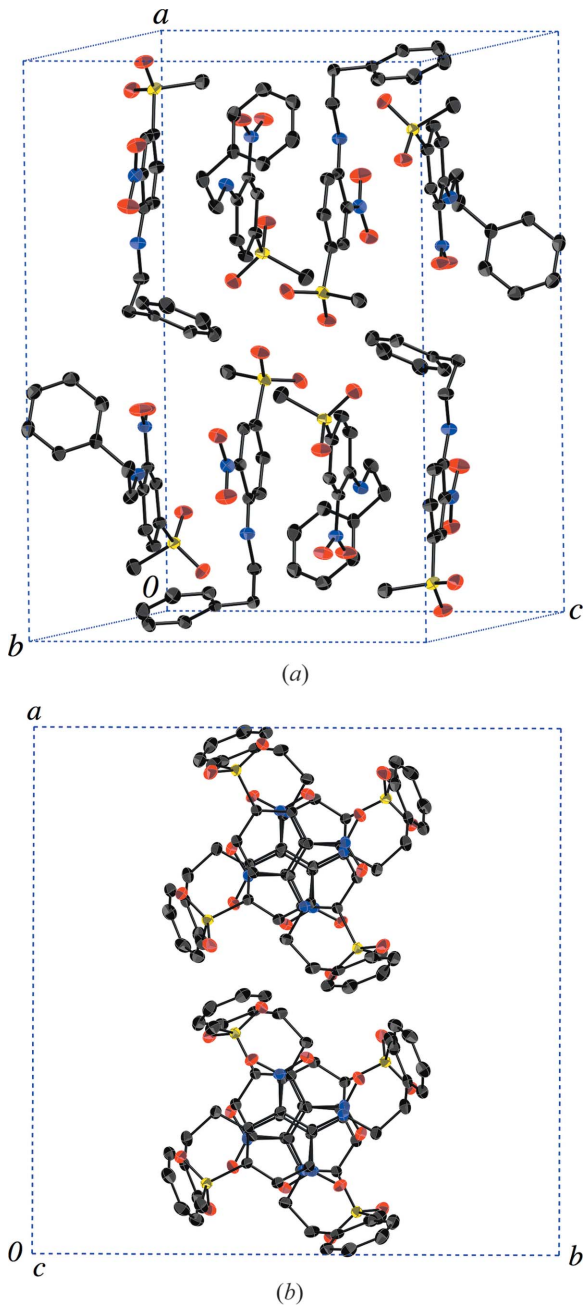


Figure 8
(*a*) A packing diagram for (IV), showing half of the 16 molecules belonging to the *I*-centred tetragonal unit cell. Note the absence of any intermolecular N—H···O hydrogen-bonding interactions. (*b*) The same eight molecules shown in part (*a*) form columns along [001] with fourfold symmetry.

However, this is still only *ca* 0.34% of the total number of surveyed organic structures. As required by the 4_1 axis, molecules of (IV) are arranged in columns along the *c* axis, with successive molecules rotated by 90° with respect to each other (Fig. 8). The aniline rings are approximately parallel and slipped somewhat. The separation between the planes is *ca* 3.7 Å, but this is apparently sufficiently favourable to take precedence over hydrogen bonding. As the views in Fig. 8 suggest, the *gauche* conformation of the ethyl group may be a key factor in making this motif possible, as the phenyl rings are positioned conveniently around the periphery of the columns.

4. Conclusions

The results of this study, taken together with those of a previous study of amine- and nitro-substituted arenes (Payne *et al.*, 2010), indicate that the introduction of changes in functionalization at a single point in the molecule can result in substantial changes in the molecular and crystal structures. In the earlier work, molecules with two amine groups and one nitro group formed hydrogen-bonded chains, while in the present work we find that molecules with a single amine group and one or two nitro groups form at most hydrogen-bonded dimers. In general, it appears that reducing the number of amine groups from two to one correlates with a reduction in the dimensionality of the hydrogen-bonding network from two (chains) to one (dimers). It is true, though, that the addition of the phenyl rings to the 2-phenylethyl groups could have played a role in this tendency towards reduced dimensionality. The structure of (III) demonstrates that N—H···N amine–cyano hydrogen bonds are preferred over N—H···O amine–nitro hydrogen bonds, so the introduction of a cyano group in these systems will result in a completely different set of intermolecular interactions. Structures (I) and (IV) show that changing a single functional group, in this case in the 4-position on the main ring, can lead to a change in the preferred conformation of the molecule, a disruption in the hydrogen-bonding pattern and a dramatically different packing structure.

Transformation of the precursors into NO release agents involves nitrosation of the amine groups, which would eliminate the intramolecular hydrogen bonding. Also, NO release agents are expected to function in an aqueous solution environment (*i.e. in vivo*). Thus, it is probably unlikely that inter- and intramolecular interactions in the solid-state structures of the precursors would correlate with the NO release behaviour. Our recent findings suggest that the characteristics of the organic group (length of alkyl chain, presence of alkyl or aryl substituents) on the former amine N atom bearing the NO group have the primary effect on the NO release rate (Yu *et al.*, 2011; Curtis *et al.*, 2013). Given this observation, it would be interesting to see how the NO release rate changes when one uses aliphatic cyclic amines of different ring sizes. Since NO leaves as a radical, it will also be of interest to see how the release rate changes when one moves from benzene derivatives to aromatic heterocycles and to larger naphthalene and anthracene-based compounds.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CU3041). Services for accessing these data are described at the back of the journal.

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supplementary materials

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A series of *N*-(2-phenylethyl)nitroaniline derivatives as precursors for slow and sustained nitric oxide release agents

Colin B. Wade, Dillip K. Mohanty, Philip J. Squattrito, Nicholas J. Amato and Kristin Kirschbaum

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2* (Bruker, 2005); data reduction: *APEX2* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2013); software used to prepare material for publication: *APEX2* (Bruker, 2005).

(C14H13N3O4) 2,4-Dinitro-*N*-(2-phenylethyl)aniline

Crystal data

$C_{14}H_{13}N_3O_4$
$M_r = 287.27$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 7.235$ (2) Å
$b = 7.282$ (2) Å
$c = 13.512$ (4) Å
$\alpha = 88.714$ (5)°
$\beta = 85.131$ (5)°
$\gamma = 67.239$ (5)°
$V = 654.0$ (4) Å^3
$Z = 2$
$F(000) = 300$
$D_x = 1.459$ Mg m^{-3}
Melting point: 425 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 11611 reflections
$\theta = 3.0$–$32.1°$
$\mu = 0.11$ mm^{-1}
$T = 100$ K
Plate, orange
0.20 × 0.10 × 0.02 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.978$, $T_{max} = 0.998$
9039 measured reflections
3158 independent reflections
2288 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 28.0°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.104$
$S = 1.03$
3158 reflections
242 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 0.1059P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O21	0.47421 (16)	0.19492 (14)	0.46231 (7)	0.0226 (3)
O22	0.30058 (15)	0.48827 (14)	0.40811 (8)	0.0218 (2)
O41	0.35861 (18)	0.39571 (17)	−0.04202 (8)	0.0288 (3)
O42	0.17704 (17)	0.61028 (16)	0.07262 (8)	0.0304 (3)
N1	0.69604 (18)	−0.09321 (17)	0.33654 (9)	0.0162 (3)
H1	0.654 (3)	−0.062 (3)	0.3982 (14)	0.032 (5)*
N2	0.41095 (17)	0.31155 (16)	0.39279 (8)	0.0150 (3)
N4	0.31213 (19)	0.44961 (18)	0.04614 (9)	0.0212 (3)
C1	0.61056 (19)	0.04072 (19)	0.26771 (10)	0.0137 (3)
C2	0.46755 (19)	0.23875 (19)	0.29173 (10)	0.0132 (3)
C3	0.3740 (2)	0.3712 (2)	0.21903 (10)	0.0141 (3)
H3	0.280 (2)	0.497 (2)	0.2391 (11)	0.018 (4)*
C4	0.4213 (2)	0.3149 (2)	0.12088 (10)	0.0166 (3)
C5	0.5681 (2)	0.1266 (2)	0.09314 (11)	0.0179 (3)
H5	0.599 (2)	0.092 (2)	0.0257 (13)	0.021 (4)*
C6	0.6582 (2)	−0.0059 (2)	0.16413 (11)	0.0167 (3)
H6	0.756 (3)	−0.133 (3)	0.1449 (13)	0.027 (4)*
C7	0.8410 (2)	−0.2971 (2)	0.31717 (12)	0.0178 (3)
H7A	0.932 (2)	−0.299 (2)	0.2580 (12)	0.018 (4)*
H7B	0.920 (2)	−0.336 (2)	0.3754 (12)	0.021 (4)*
C8	0.7394 (2)	−0.4436 (2)	0.30299 (12)	0.0169 (3)
H8B	0.641 (2)	−0.429 (2)	0.3592 (12)	0.015 (4)*
H8A	0.662 (2)	−0.411 (2)	0.2453 (12)	0.014 (4)*
C9	0.8931 (2)	−0.65607 (19)	0.29443 (10)	0.0151 (3)
C10	0.9689 (2)	−0.7611 (2)	0.37972 (11)	0.0185 (3)
H10	0.917 (2)	−0.699 (2)	0.4453 (13)	0.025 (4)*
C11	1.1134 (2)	−0.9552 (2)	0.37235 (13)	0.0221 (3)
H11	1.161 (3)	−1.025 (3)	0.4326 (14)	0.034 (5)*
C12	1.1825 (2)	−1.0461 (2)	0.27972 (13)	0.0237 (3)
H12	1.277 (3)	−1.178 (3)	0.2770 (12)	0.026 (4)*
C13	1.1069 (2)	−0.9442 (2)	0.19510 (12)	0.0225 (3)
H13	1.155 (3)	−1.014 (3)	0.1310 (14)	0.031 (5)*
C14	0.9635 (2)	−0.7496 (2)	0.20191 (11)	0.0182 (3)

H14	0.914 (2)	−0.682 (2)	0.1425 (13)	0.025 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O21	0.0317 (6)	0.0159 (5)	0.0157 (5)	−0.0043 (4)	−0.0026 (4)	0.0024 (4)
O22	0.0234 (6)	0.0124 (5)	0.0224 (5)	0.0007 (4)	0.0012 (4)	−0.0048 (4)
O41	0.0441 (7)	0.0303 (6)	0.0144 (5)	−0.0161 (5)	−0.0063 (5)	0.0025 (4)
O42	0.0346 (7)	0.0196 (6)	0.0282 (6)	−0.0002 (5)	−0.0069 (5)	0.0043 (5)
N1	0.0168 (6)	0.0101 (6)	0.0190 (6)	−0.0023 (5)	−0.0014 (5)	−0.0008 (5)
N2	0.0154 (6)	0.0131 (6)	0.0154 (6)	−0.0046 (5)	−0.0004 (5)	−0.0009 (5)
N4	0.0282 (7)	0.0195 (7)	0.0180 (6)	−0.0109 (6)	−0.0052 (5)	0.0036 (5)
C1	0.0113 (6)	0.0122 (6)	0.0191 (7)	−0.0061 (5)	−0.0008 (5)	−0.0012 (5)
C2	0.0140 (7)	0.0112 (6)	0.0143 (7)	−0.0050 (5)	0.0010 (5)	−0.0027 (5)
C3	0.0129 (6)	0.0108 (6)	0.0186 (7)	−0.0047 (5)	0.0002 (5)	−0.0014 (5)
C4	0.0182 (7)	0.0151 (7)	0.0180 (7)	−0.0080 (6)	−0.0021 (6)	0.0020 (5)
C5	0.0217 (7)	0.0183 (7)	0.0155 (7)	−0.0104 (6)	0.0029 (6)	−0.0045 (6)
C6	0.0152 (7)	0.0127 (7)	0.0214 (7)	−0.0049 (6)	0.0028 (6)	−0.0047 (5)
C7	0.0135 (7)	0.0108 (7)	0.0263 (8)	−0.0011 (5)	−0.0042 (6)	−0.0003 (6)
C8	0.0130 (7)	0.0121 (7)	0.0235 (8)	−0.0024 (5)	−0.0018 (6)	−0.0014 (5)
C9	0.0119 (6)	0.0126 (7)	0.0214 (7)	−0.0055 (5)	−0.0002 (5)	−0.0017 (5)
C10	0.0188 (7)	0.0167 (7)	0.0203 (8)	−0.0077 (6)	−0.0003 (6)	0.0010 (6)
C11	0.0190 (8)	0.0156 (7)	0.0326 (9)	−0.0073 (6)	−0.0052 (6)	0.0062 (6)
C12	0.0138 (7)	0.0110 (7)	0.0451 (10)	−0.0040 (6)	0.0009 (6)	−0.0032 (6)
C13	0.0172 (7)	0.0196 (7)	0.0311 (9)	−0.0088 (6)	0.0068 (6)	−0.0120 (6)
C14	0.0177 (7)	0.0188 (7)	0.0200 (7)	−0.0091 (6)	−0.0007 (6)	−0.0021 (6)

Geometric parameters (Å, º)

O21—N2	1.2448 (15)	C7—C8	1.534 (2)
O22—N2	1.2350 (14)	C7—H7A	0.989 (16)
O41—N4	1.2398 (16)	C7—H7B	0.984 (16)
O42—N4	1.2356 (16)	C8—C9	1.5161 (19)
N1—C1	1.3374 (18)	C8—H8B	0.974 (16)
N1—C7	1.4622 (17)	C8—H8A	0.967 (16)
N1—H1	0.867 (19)	C9—C14	1.396 (2)
N2—C2	1.4433 (17)	C9—C10	1.399 (2)
N4—C4	1.4482 (18)	C10—C11	1.395 (2)
C1—C6	1.429 (2)	C10—H10	0.980 (17)
C1—C2	1.4369 (18)	C11—C12	1.389 (2)
C2—C3	1.3850 (19)	C11—H11	0.966 (19)
C3—C4	1.372 (2)	C12—C13	1.382 (2)
C3—H3	0.932 (16)	C12—H12	0.938 (17)
C4—C5	1.406 (2)	C13—C14	1.395 (2)
C5—C6	1.362 (2)	C13—H13	0.979 (18)
C5—H5	0.937 (17)	C14—H14	0.955 (17)
C6—H6	0.948 (17)		
C1—N1—C7	125.87 (13)	C8—C7—H7A	110.3 (9)
C1—N1—H1	117.6 (12)	N1—C7—H7B	106.3 (9)

C7—N1—H1	116.2 (12)	C8—C7—H7B	109.5 (9)
O22—N2—O21	121.63 (11)	H7A—C7—H7B	108.7 (13)
O22—N2—C2	119.07 (11)	C9—C8—C7	111.05 (11)
O21—N2—C2	119.30 (11)	C9—C8—H8B	110.6 (9)
O42—N4—O41	123.20 (12)	C7—C8—H8B	108.5 (9)
O42—N4—C4	119.13 (12)	C9—C8—H8A	110.1 (9)
O41—N4—C4	117.66 (12)	C7—C8—H8A	111.3 (9)
N1—C1—C6	121.24 (12)	H8B—C8—H8A	105.1 (12)
N1—C1—C2	123.14 (12)	C14—C9—C10	118.80 (13)
C6—C1—C2	115.62 (12)	C14—C9—C8	120.97 (13)
C3—C2—C1	121.89 (12)	C10—C9—C8	120.23 (13)
C3—C2—N2	115.84 (11)	C11—C10—C9	120.58 (14)
C1—C2—N2	122.28 (12)	C11—C10—H10	119.7 (10)
C4—C3—C2	119.61 (12)	C9—C10—H10	119.7 (10)
C4—C3—H3	122.3 (9)	C12—C11—C10	119.96 (15)
C2—C3—H3	118.1 (9)	C12—C11—H11	121.3 (11)
C3—C4—C5	120.74 (13)	C10—C11—H11	118.7 (11)
C3—C4—N4	118.95 (12)	C13—C12—C11	119.87 (14)
C5—C4—N4	120.27 (12)	C13—C12—H12	121.9 (11)
C6—C5—C4	120.01 (13)	C11—C12—H12	118.2 (11)
C6—C5—H5	120.6 (10)	C12—C13—C14	120.46 (14)
C4—C5—H5	119.3 (10)	C12—C13—H13	118.1 (10)
C5—C6—C1	122.00 (13)	C14—C13—H13	121.4 (10)
C5—C6—H6	119.6 (10)	C13—C14—C9	120.33 (14)
C1—C6—H6	118.4 (10)	C13—C14—H14	119.1 (10)
N1—C7—C8	112.67 (12)	C9—C14—H14	120.6 (10)
N1—C7—H7A	109.2 (9)		

C7—N1—C1—C6	−0.9 (2)	C3—C4—C5—C6	3.2 (2)
C7—N1—C1—C2	179.47 (12)	N4—C4—C5—C6	−174.48 (13)
N1—C1—C2—C3	−176.80 (13)	C4—C5—C6—C1	−0.9 (2)
C6—C1—C2—C3	3.52 (19)	N1—C1—C6—C5	177.98 (13)
N1—C1—C2—N2	2.6 (2)	C2—C1—C6—C5	−2.33 (19)
C6—C1—C2—N2	−177.05 (12)	C1—N1—C7—C8	−85.52 (17)
O22—N2—C2—C3	−6.70 (18)	N1—C7—C8—C9	−173.75 (12)
O21—N2—C2—C3	173.22 (12)	C7—C8—C9—C14	−99.44 (16)
O22—N2—C2—C1	173.85 (12)	C7—C8—C9—C10	79.65 (16)
O21—N2—C2—C1	−6.24 (18)	C14—C9—C10—C11	0.4 (2)
C1—C2—C3—C4	−1.4 (2)	C8—C9—C10—C11	−178.69 (13)
N2—C2—C3—C4	179.12 (12)	C9—C10—C11—C12	−0.2 (2)
C2—C3—C4—C5	−2.0 (2)	C10—C11—C12—C13	−0.4 (2)
C2—C3—C4—N4	175.69 (12)	C11—C12—C13—C14	0.9 (2)
O42—N4—C4—C3	−1.2 (2)	C12—C13—C14—C9	−0.7 (2)
O41—N4—C4—C3	179.53 (13)	C10—C9—C14—C13	0.0 (2)
O42—N4—C4—C5	176.52 (13)	C8—C9—C14—C13	179.15 (13)
O41—N4—C4—C5	−2.7 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.867 (19)	1.983 (19)	2.6377 (16)	131.5 (16)
N1—H1···O21^{i}	0.867 (19)	2.381 (19)	3.0823 (18)	138.3 (16)

Symmetry code: (i) −*x*+1, −*y*, −*z*+1.

(C22H22N4O4) 4,6-Dinitro-*N*,*N*′-bis(2-phenylethyl)benzene-1,3-diamine

Crystal data

$C_{22}H_{22}N_4O_4$
M_r = 406.44
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 8.1121 (7) Å
b = 10.1819 (8) Å
c = 13.1018 (11) Å
α = 93.466 (1)°
β = 106.595 (1)°
γ = 106.932 (1)°
V = 979.88 (14) Å^3
Z = 2
$F(000)$ = 428
D_x = 1.378 Mg m^{-3}
Melting point: 408 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 17364 reflections
θ = 2.5–32.7°
μ = 0.10 mm^{-1}
T = 100 K
Parallelpiped, orange
0.20 × 0.10 × 0.05 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.981, T_{max} = 0.995
17364 measured reflections
6868 independent reflections
5289 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 33.0°, θ_{min} = 1.6°
h = −12→12
k = −15→15
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.121
S = 1.03
6868 reflections
359 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0693P)^2 + 0.148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.57 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O21	0.23044 (11)	0.49365 (8)	−0.03714 (6)	0.02254 (17)
O22	0.20579 (10)	0.44974 (8)	0.11874 (6)	0.02074 (16)
O41	0.80203 (11)	0.91022 (8)	0.45448 (6)	0.02101 (16)
O42	0.57135 (10)	0.72779 (8)	0.43962 (6)	0.02098 (16)
N1	0.51043 (11)	0.69381 (9)	−0.05088 (6)	0.01446 (15)
H1	0.410 (2)	0.6227 (15)	−0.0847 (12)	0.029 (4)*
N2	0.28480 (11)	0.52119 (8)	0.06328 (7)	0.01512 (16)
N4	0.67006 (11)	0.80913 (9)	0.39872 (6)	0.01476 (16)
N5	0.86876 (11)	1.00007 (8)	0.28122 (7)	0.01354 (15)
H5	0.905 (2)	1.0156 (17)	0.3538 (14)	0.039 (4)*
C1	0.54668 (12)	0.72552 (9)	0.05682 (7)	0.01225 (16)
C2	0.44289 (12)	0.63957 (9)	0.11528 (7)	0.01285 (16)
C3	0.48939 (12)	0.67177 (9)	0.22604 (7)	0.01303 (16)
H3	0.4177 (19)	0.6132 (15)	0.2631 (11)	0.026 (4)*
C4	0.63377 (12)	0.78684 (9)	0.28394 (7)	0.01247 (16)
C5	0.73706 (12)	0.88063 (9)	0.22938 (7)	0.01228 (16)
C6	0.69047 (12)	0.84309 (9)	0.11745 (7)	0.01281 (16)
H6	0.7613 (18)	0.9005 (14)	0.0809 (11)	0.020 (3)*
C7	0.60110 (13)	0.78288 (10)	−0.11463 (8)	0.01417 (17)
H7A	0.5825 (17)	0.7264 (13)	−0.1818 (10)	0.015 (3)*
H7B	0.7300 (18)	0.8193 (13)	−0.0770 (10)	0.017 (3)*
C8	0.52363 (14)	0.90188 (11)	−0.14096 (8)	0.01701 (18)
H8B	0.5228 (19)	0.9459 (15)	−0.0728 (12)	0.025 (4)*
H8A	0.396 (2)	0.8610 (15)	−0.1902 (12)	0.027 (4)*
C9	0.63215 (12)	1.00500 (10)	−0.19438 (7)	0.01360 (17)
C10	0.59759 (13)	0.98259 (10)	−0.30591 (8)	0.01541 (17)
H10	0.501 (2)	0.9015 (16)	−0.3492 (12)	0.029 (4)*
C11	0.70127 (14)	1.07599 (11)	−0.35487 (8)	0.01895 (19)
H11	0.677 (2)	1.0608 (16)	−0.4351 (13)	0.032 (4)*
C12	0.84093 (14)	1.19286 (11)	−0.29268 (9)	0.0209 (2)
H12	0.915 (2)	1.2594 (18)	−0.3244 (14)	0.042 (4)*
C13	0.87739 (14)	1.21631 (11)	−0.18180 (9)	0.0208 (2)
H13	0.974 (2)	1.2986 (18)	−0.1407 (14)	0.039 (4)*
C14	0.77321 (14)	1.12241 (10)	−0.13291 (8)	0.01714 (18)
H14	0.796 (2)	1.1411 (16)	−0.0549 (13)	0.031 (4)*
C15	0.97367 (13)	1.09930 (10)	0.22897 (8)	0.01359 (16)
H15A	1.0524 (17)	1.0589 (13)	0.2021 (10)	0.013 (3)*
H15B	0.8901 (18)	1.1204 (14)	0.1646 (11)	0.019 (3)*
C16	1.08512 (12)	1.23457 (10)	0.30761 (8)	0.01436 (17)
H16B	1.1659 (18)	1.2924 (14)	0.2730 (11)	0.021 (3)*
H16A	1.1643 (18)	1.2117 (14)	0.3725 (11)	0.022 (3)*
C17	0.96790 (12)	1.31233 (9)	0.33662 (7)	0.01351 (17)
C18	0.90244 (13)	1.28766 (10)	0.42395 (8)	0.01619 (18)
H18	0.9416 (18)	1.2227 (14)	0.4720 (11)	0.021 (3)*
C19	0.78662 (14)	1.35502 (11)	0.44617 (8)	0.01860 (19)
H19	0.7421 (18)	1.3349 (14)	0.5078 (11)	0.022 (3)*
C20	0.73618 (14)	1.44989 (11)	0.38173 (9)	0.01931 (19)

H20	0.658 (2)	1.4978 (15)	0.4001 (12)	0.028 (4)*
C21	0.80260 (14)	1.47698 (10)	0.29578 (8)	0.01828 (19)
H21	0.7735 (19)	1.5465 (15)	0.2518 (12)	0.024 (3)*
C22	0.91731 (13)	1.40873 (10)	0.27311 (8)	0.01578 (18)
H22	0.9588 (18)	1.4296 (14)	0.2116 (11)	0.019 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O21	0.0230 (4)	0.0213 (4)	0.0153 (3)	−0.0007 (3)	0.0019 (3)	0.0029 (3)
O22	0.0209 (4)	0.0182 (3)	0.0231 (4)	0.0014 (3)	0.0112 (3)	0.0063 (3)
O41	0.0254 (4)	0.0195 (3)	0.0137 (3)	0.0027 (3)	0.0045 (3)	0.0013 (3)
O42	0.0231 (4)	0.0255 (4)	0.0163 (3)	0.0058 (3)	0.0102 (3)	0.0083 (3)
N1	0.0166 (4)	0.0142 (3)	0.0116 (3)	0.0029 (3)	0.0051 (3)	0.0021 (3)
N2	0.0149 (4)	0.0137 (3)	0.0168 (4)	0.0042 (3)	0.0053 (3)	0.0036 (3)
N4	0.0178 (4)	0.0165 (4)	0.0129 (3)	0.0083 (3)	0.0062 (3)	0.0043 (3)
N5	0.0148 (4)	0.0133 (3)	0.0123 (3)	0.0037 (3)	0.0048 (3)	0.0025 (3)
C1	0.0134 (4)	0.0130 (4)	0.0128 (4)	0.0063 (3)	0.0053 (3)	0.0037 (3)
C2	0.0125 (4)	0.0123 (4)	0.0138 (4)	0.0038 (3)	0.0042 (3)	0.0030 (3)
C3	0.0139 (4)	0.0136 (4)	0.0147 (4)	0.0066 (3)	0.0064 (3)	0.0047 (3)
C4	0.0150 (4)	0.0141 (4)	0.0107 (4)	0.0067 (3)	0.0054 (3)	0.0035 (3)
C5	0.0127 (4)	0.0126 (4)	0.0136 (4)	0.0064 (3)	0.0047 (3)	0.0032 (3)
C6	0.0139 (4)	0.0137 (4)	0.0127 (4)	0.0049 (3)	0.0064 (3)	0.0032 (3)
C7	0.0157 (4)	0.0159 (4)	0.0130 (4)	0.0061 (3)	0.0065 (3)	0.0037 (3)
C8	0.0165 (4)	0.0198 (4)	0.0201 (4)	0.0090 (4)	0.0097 (4)	0.0083 (4)
C9	0.0130 (4)	0.0148 (4)	0.0160 (4)	0.0070 (3)	0.0060 (3)	0.0043 (3)
C10	0.0148 (4)	0.0148 (4)	0.0155 (4)	0.0041 (3)	0.0038 (3)	0.0021 (3)
C11	0.0209 (5)	0.0220 (5)	0.0179 (4)	0.0090 (4)	0.0093 (4)	0.0066 (4)
C12	0.0181 (4)	0.0186 (4)	0.0304 (5)	0.0069 (4)	0.0121 (4)	0.0101 (4)
C13	0.0149 (4)	0.0137 (4)	0.0306 (5)	0.0034 (3)	0.0043 (4)	0.0010 (4)
C14	0.0174 (4)	0.0180 (4)	0.0156 (4)	0.0080 (4)	0.0028 (3)	0.0007 (3)
C15	0.0138 (4)	0.0142 (4)	0.0147 (4)	0.0052 (3)	0.0064 (3)	0.0038 (3)
C16	0.0123 (4)	0.0152 (4)	0.0151 (4)	0.0039 (3)	0.0041 (3)	0.0029 (3)
C17	0.0126 (4)	0.0125 (4)	0.0134 (4)	0.0027 (3)	0.0026 (3)	0.0008 (3)
C18	0.0176 (4)	0.0150 (4)	0.0154 (4)	0.0041 (3)	0.0054 (3)	0.0030 (3)
C19	0.0195 (4)	0.0186 (4)	0.0178 (4)	0.0045 (4)	0.0081 (4)	0.0013 (3)
C20	0.0177 (4)	0.0177 (4)	0.0221 (5)	0.0066 (4)	0.0057 (4)	−0.0016 (4)
C21	0.0192 (4)	0.0155 (4)	0.0191 (4)	0.0067 (4)	0.0035 (4)	0.0021 (3)
C22	0.0170 (4)	0.0154 (4)	0.0145 (4)	0.0049 (3)	0.0045 (3)	0.0030 (3)

Geometric parameters (Å, º)

O21—N2	1.2475 (11)	C9—C10	1.3980 (13)
O22—N2	1.2354 (10)	C10—C11	1.3925 (13)
O41—N4	1.2489 (11)	C10—H10	0.966 (15)
O42—N4	1.2356 (10)	C11—C12	1.3905 (15)
N1—C1	1.3544 (12)	C11—H11	1.006 (16)
N1—C7	1.4543 (12)	C12—C13	1.3880 (16)
N1—H1	0.891 (15)	C12—H12	0.965 (17)
N2—C2	1.4363 (12)	C13—C14	1.3968 (15)

N4—C4	1.4376 (12)	C13—H13	0.963 (17)
N5—C5	1.3456 (12)	C14—H14	0.980 (16)
N5—C15	1.4592 (12)	C15—C16	1.5320 (13)
N5—H5	0.900 (17)	C15—H15A	0.983 (13)
C1—C6	1.4025 (13)	C15—H15B	0.999 (13)
C1—C2	1.4428 (12)	C16—C17	1.5113 (13)
C2—C3	1.3832 (13)	C16—H16B	0.979 (14)
C3—C4	1.3805 (13)	C16—H16A	0.994 (14)
C3—H3	0.961 (14)	C17—C18	1.3995 (13)
C4—C5	1.4434 (12)	C17—C22	1.4009 (13)
C5—C6	1.4039 (13)	C18—C19	1.3948 (14)
C6—H6	0.947 (14)	C18—H18	0.996 (14)
C7—C8	1.5337 (14)	C19—C20	1.3945 (15)
C7—H7A	0.969 (13)	C19—H19	0.983 (14)
C7—H7B	0.965 (13)	C20—C21	1.3900 (15)
C8—C9	1.5065 (13)	C20—H20	0.974 (15)
C8—H8B	0.977 (14)	C21—C22	1.3952 (14)
C8—H8A	1.000 (15)	C21—H21	0.978 (14)
C9—C14	1.3956 (13)	C22—H22	0.971 (13)

C1—N1—C7	124.07 (8)	C11—C10—C9	120.67 (9)
C1—N1—H1	115.8 (10)	C11—C10—H10	119.9 (9)
C7—N1—H1	119.0 (10)	C9—C10—H10	119.4 (9)
O22—N2—O21	121.71 (8)	C12—C11—C10	119.99 (9)
O22—N2—C2	119.42 (8)	C12—C11—H11	118.8 (9)
O21—N2—C2	118.88 (8)	C10—C11—H11	121.2 (9)
O42—N4—O41	121.81 (8)	C13—C12—C11	120.05 (9)
O42—N4—C4	119.44 (8)	C13—C12—H12	118.1 (10)
O41—N4—C4	118.75 (8)	C11—C12—H12	121.8 (10)
C5—N5—C15	124.42 (8)	C12—C13—C14	119.84 (9)
C5—N5—H5	118.4 (10)	C12—C13—H13	118.5 (10)
C15—N5—H5	116.8 (10)	C14—C13—H13	121.7 (10)
N1—C1—C6	121.20 (8)	C9—C14—C13	120.72 (9)
N1—C1—C2	122.14 (8)	C9—C14—H14	119.6 (9)
C6—C1—C2	116.66 (8)	C13—C14—H14	119.6 (9)
C3—C2—N2	116.57 (8)	N5—C15—C16	110.11 (8)
C3—C2—C1	120.46 (8)	N5—C15—H15A	110.3 (7)
N2—C2—C1	122.94 (8)	C16—C15—H15A	111.1 (7)
C4—C3—C2	121.62 (8)	N5—C15—H15B	109.9 (8)
C4—C3—H3	119.5 (8)	C16—C15—H15B	108.9 (8)
C2—C3—H3	118.9 (9)	H15A—C15—H15B	106.3 (11)
C3—C4—N4	116.64 (8)	C17—C16—C15	112.77 (8)
C3—C4—C5	120.48 (8)	C17—C16—H16B	109.9 (8)
N4—C4—C5	122.85 (8)	C15—C16—H16B	107.2 (8)
N5—C5—C6	120.81 (8)	C17—C16—H16A	111.8 (8)
N5—C5—C4	122.58 (8)	C15—C16—H16A	108.2 (8)
C6—C5—C4	116.58 (8)	H16B—C16—H16A	106.7 (11)
C1—C6—C5	124.07 (8)	C18—C17—C22	118.37 (9)
C1—C6—H6	118.1 (8)	C18—C17—C16	121.76 (8)

C5—C6—H6	117.8 (8)	C22—C17—C16	119.84 (8)
N1—C7—C8	111.96 (8)	C19—C18—C17	121.00 (9)
N1—C7—H7A	107.9 (7)	C19—C18—H18	119.6 (8)
C8—C7—H7A	108.4 (8)	C17—C18—H18	119.4 (8)
N1—C7—H7B	109.8 (8)	C20—C19—C18	120.00 (9)
C8—C7—H7B	110.4 (8)	C20—C19—H19	121.0 (8)
H7A—C7—H7B	108.2 (11)	C18—C19—H19	119.0 (8)
C9—C8—C7	112.29 (8)	C21—C20—C19	119.56 (9)
C9—C8—H8B	111.3 (8)	C21—C20—H20	121.8 (9)
C7—C8—H8B	106.6 (8)	C19—C20—H20	118.6 (9)
C9—C8—H8A	109.2 (8)	C20—C21—C22	120.38 (9)
C7—C8—H8A	108.3 (8)	C20—C21—H21	120.7 (8)
H8B—C8—H8A	109.0 (12)	C22—C21—H21	118.8 (8)
C14—C9—C10	118.74 (9)	C21—C22—C17	120.68 (9)
C14—C9—C8	120.54 (9)	C21—C22—H22	117.6 (8)
C10—C9—C8	120.69 (9)	C17—C22—H22	121.7 (8)
C7—N1—C1—C6	−6.57 (14)	N5—C5—C6—C1	−175.36 (8)
C7—N1—C1—C2	174.69 (8)	C4—C5—C6—C1	3.10 (13)
O22—N2—C2—C3	−4.46 (12)	C1—N1—C7—C8	−79.33 (11)
O21—N2—C2—C3	175.24 (8)	N1—C7—C8—C9	172.60 (8)
O22—N2—C2—C1	177.78 (8)	C7—C8—C9—C14	−92.60 (11)
O21—N2—C2—C1	−2.53 (13)	C7—C8—C9—C10	85.24 (11)
N1—C1—C2—C3	176.93 (8)	C14—C9—C10—C11	−0.33 (14)
C6—C1—C2—C3	−1.86 (13)	C8—C9—C10—C11	−178.21 (9)
N1—C1—C2—N2	−5.39 (14)	C9—C10—C11—C12	0.07 (15)
C6—C1—C2—N2	175.82 (8)	C10—C11—C12—C13	0.16 (15)
N2—C2—C3—C4	−177.06 (8)	C11—C12—C13—C14	−0.14 (15)
C1—C2—C3—C4	0.76 (14)	C10—C9—C14—C13	0.36 (14)
C2—C3—C4—N4	−179.52 (8)	C8—C9—C14—C13	178.24 (9)
C2—C3—C4—C5	2.36 (13)	C12—C13—C14—C9	−0.13 (15)
O42—N4—C4—C3	−1.13 (12)	C5—N5—C15—C16	169.34 (8)
O41—N4—C4—C3	178.37 (8)	N5—C15—C16—C17	−66.94 (10)
O42—N4—C4—C5	176.93 (8)	C15—C16—C17—C18	89.20 (11)
O41—N4—C4—C5	−3.57 (13)	C15—C16—C17—C22	−88.67 (10)
C15—N5—C5—C6	−0.22 (13)	C22—C17—C18—C19	1.31 (14)
C15—N5—C5—C4	−178.58 (8)	C16—C17—C18—C19	−176.60 (9)
C3—C4—C5—N5	174.25 (8)	C17—C18—C19—C20	−0.80 (15)
N4—C4—C5—N5	−3.74 (13)	C18—C19—C20—C21	−0.24 (15)
C3—C4—C5—C6	−4.17 (13)	C19—C20—C21—C22	0.74 (15)
N4—C4—C5—C6	177.83 (8)	C20—C21—C22—C17	−0.22 (15)
N1—C1—C6—C5	−178.97 (8)	C18—C17—C22—C21	−0.80 (14)
C2—C1—C6—C5	−0.17 (13)	C16—C17—C22—C21	177.15 (9)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.891 (15)	1.935 (15)	2.6318 (11)	133.8 (13)

N5—H5···O41	0.900 (17)	1.967 (16)	2.6358 (11)	129.8 (14)
N5—H5···O41^{i}	0.900 (17)	2.800 (17)	3.5877 (11)	146.8 (13)

Symmetry code: (i) −*x*+2, −*y*+2, −*z*+1.

(C15H13N3O2) 2-cyano-4-nitro-*N*-(2-phenylethyl)aniline

Crystal data

$C_{15}H_{13}N_3O_2$
M_r = 267.28
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 7.4871 (5) Å
b = 16.270 (1) Å
c = 10.8432 (7) Å
β = 94.384 (1)°
V = 1317.00 (15) Å^3
Z = 4
$F(000)$ = 560
D_x = 1.348 Mg m^{-3}
Melting point: 427 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 23429 reflections
θ = 2.3–33.0°
μ = 0.09 mm^{-1}
T = 100 K
Parallelpiped, yellow
0.40 × 0.20 × 0.10 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer
Radiation source: sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.964, T_{max} = 0.991
23007 measured reflections
4732 independent reflections
4189 reflections with $I > 2\sigma(I)$
R_{int} = 0.018
θ_{max} = 32.9°, θ_{min} = 2.3°
h = −11→11
k = −24→24
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.113
S = 1.04
4732 reflections
233 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0687P)^2 + 0.3103P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O41	0.28684 (9)	0.12353 (4)	0.29556 (6)	0.02323 (14)

O42	0.10504 (8)	0.03747 (4)	0.37421 (6)	0.02067 (13)
N1	0.65662 (8)	0.09507 (4)	0.83376 (6)	0.01439 (12)
H1	0.6214 (19)	0.0666 (9)	0.8948 (14)	0.033 (3)*
N2	0.33192 (10)	−0.05113 (4)	0.89432 (7)	0.02022 (14)
N4	0.23997 (8)	0.08139 (4)	0.38232 (6)	0.01466 (13)
C1	0.55906 (9)	0.09106 (4)	0.72443 (6)	0.01199 (13)
C2	0.40849 (9)	0.03712 (4)	0.70702 (6)	0.01168 (13)
C3	0.30296 (9)	0.03411 (4)	0.59568 (7)	0.01221 (13)
H3	0.2029 (15)	−0.0007 (7)	0.5865 (11)	0.019 (3)*
C4	0.34763 (9)	0.08426 (4)	0.49902 (6)	0.01264 (13)
C5	0.49621 (10)	0.13679 (5)	0.51165 (7)	0.01499 (14)
H5	0.5272 (16)	0.1712 (8)	0.4445 (11)	0.021 (3)*
C6	0.59954 (10)	0.13990 (5)	0.62209 (7)	0.01514 (14)
H6	0.6992 (17)	0.1754 (8)	0.6296 (12)	0.024 (3)*
C7	0.80953 (9)	0.14949 (5)	0.86030 (7)	0.01465 (14)
H7A	0.7833 (16)	0.2054 (7)	0.8259 (11)	0.020 (3)*
H7B	0.8227 (16)	0.1545 (8)	0.9503 (12)	0.022 (3)*
C8	0.98355 (10)	0.11550 (5)	0.81298 (8)	0.01875 (15)
H8B	0.9959 (18)	0.0584 (8)	0.8430 (13)	0.029 (3)*
H8A	0.9744 (18)	0.1137 (8)	0.7233 (13)	0.030 (3)*
C9	1.14367 (9)	0.16670 (5)	0.85827 (7)	0.01476 (14)
C10	1.22232 (10)	0.15533 (5)	0.97834 (7)	0.01569 (14)
H10	1.1749 (18)	0.1134 (8)	1.0314 (13)	0.027 (3)*
C11	1.36857 (10)	0.20255 (5)	1.02246 (7)	0.01573 (14)
H11	1.4201 (18)	0.1936 (8)	1.1055 (12)	0.026 (3)*
C12	1.43693 (10)	0.26274 (5)	0.94762 (7)	0.01653 (14)
H12	1.5371 (18)	0.2976 (8)	0.9811 (13)	0.030 (3)*
C13	1.36012 (10)	0.27489 (5)	0.82797 (7)	0.01769 (15)
H13	1.4088 (18)	0.3160 (8)	0.7747 (13)	0.028 (3)*
C14	1.21486 (10)	0.22666 (5)	0.78384 (7)	0.01678 (14)
H14	1.1657 (16)	0.2334 (8)	0.6966 (12)	0.024 (3)*
C15	0.36369 (9)	−0.01308 (4)	0.80896 (7)	0.01396 (13)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O41	0.0262 (3)	0.0287 (3)	0.0145 (3)	−0.0025 (2)	−0.0005 (2)	0.0067 (2)
O42	0.0176 (3)	0.0243 (3)	0.0194 (3)	−0.0046 (2)	−0.0032 (2)	−0.0013 (2)
N1	0.0130 (3)	0.0174 (3)	0.0126 (3)	−0.0041 (2)	−0.0002 (2)	0.0009 (2)
N2	0.0213 (3)	0.0208 (3)	0.0186 (3)	−0.0022 (2)	0.0014 (2)	0.0046 (2)
N4	0.0147 (3)	0.0157 (3)	0.0134 (3)	0.0021 (2)	0.0001 (2)	−0.0006 (2)
C1	0.0101 (3)	0.0129 (3)	0.0131 (3)	−0.0004 (2)	0.0014 (2)	0.0003 (2)
C2	0.0109 (3)	0.0117 (3)	0.0126 (3)	−0.0003 (2)	0.0017 (2)	0.0009 (2)
C3	0.0109 (3)	0.0123 (3)	0.0135 (3)	0.0000 (2)	0.0014 (2)	−0.0001 (2)
C4	0.0119 (3)	0.0141 (3)	0.0118 (3)	0.0008 (2)	0.0001 (2)	0.0006 (2)
C5	0.0142 (3)	0.0161 (3)	0.0148 (3)	−0.0016 (2)	0.0018 (2)	0.0030 (2)
C6	0.0131 (3)	0.0172 (3)	0.0152 (3)	−0.0040 (2)	0.0012 (2)	0.0026 (2)
C7	0.0120 (3)	0.0162 (3)	0.0157 (3)	−0.0023 (2)	0.0002 (2)	−0.0024 (2)
C8	0.0123 (3)	0.0198 (3)	0.0238 (4)	−0.0008 (2)	−0.0008 (3)	−0.0089 (3)
C9	0.0105 (3)	0.0159 (3)	0.0178 (3)	0.0012 (2)	0.0001 (2)	−0.0052 (2)

C10	0.0148 (3)	0.0147 (3)	0.0175 (3)	−0.0009 (2)	0.0006 (2)	−0.0014 (2)
C11	0.0140 (3)	0.0173 (3)	0.0155 (3)	0.0000 (2)	−0.0012 (2)	−0.0019 (2)
C12	0.0128 (3)	0.0176 (3)	0.0189 (3)	−0.0020 (2)	−0.0001 (2)	−0.0022 (3)
C13	0.0161 (3)	0.0190 (3)	0.0181 (3)	−0.0004 (2)	0.0022 (3)	0.0010 (3)
C14	0.0142 (3)	0.0208 (3)	0.0151 (3)	0.0027 (2)	−0.0006 (2)	−0.0022 (3)
C15	0.0126 (3)	0.0137 (3)	0.0154 (3)	−0.0012 (2)	0.0003 (2)	0.0001 (2)

Geometric parameters (Å, º)

O41—N4	1.2364 (9)	C7—C8	1.5391 (11)
O42—N4	1.2351 (9)	C7—H7A	0.997 (12)
N1—C1	1.3456 (9)	C7—H7B	0.976 (13)
N1—C7	1.4585 (9)	C8—C9	1.5107 (10)
N1—H1	0.866 (15)	C8—H8B	0.986 (14)
N2—C15	1.1534 (10)	C8—H8A	0.970 (14)
N4—C4	1.4481 (9)	C9—C14	1.3975 (11)
C1—C6	1.4163 (10)	C9—C10	1.3995 (11)
C1—C2	1.4298 (9)	C10—C11	1.3921 (10)
C2—C3	1.3923 (10)	C10—H10	0.977 (13)
C2—C15	1.4346 (10)	C11—C12	1.3938 (11)
C3—C4	1.3892 (10)	C11—H11	0.963 (13)
C3—H3	0.938 (12)	C12—C13	1.3925 (11)
C4—C5	1.4013 (10)	C12—H12	0.987 (14)
C5—C6	1.3761 (10)	C13—C14	1.3957 (11)
C5—H5	0.961 (12)	C13—H13	0.972 (14)
C6—H6	0.942 (13)	C14—H14	0.994 (13)
C1—N1—C7	124.63 (6)	C8—C7—H7B	109.9 (7)
C1—N1—H1	118.1 (10)	H7A—C7—H7B	107.4 (10)
C7—N1—H1	117.0 (10)	C9—C8—C7	111.37 (6)
O42—N4—O41	123.01 (7)	C9—C8—H8B	111.1 (8)
O42—N4—C4	118.59 (6)	C7—C8—H8B	106.8 (8)
O41—N4—C4	118.40 (6)	C9—C8—H8A	109.7 (8)
N1—C1—C6	121.93 (6)	C7—C8—H8A	110.4 (8)
N1—C1—C2	121.03 (6)	H8B—C8—H8A	107.4 (11)
C6—C1—C2	117.04 (6)	C14—C9—C10	118.53 (7)
C3—C2—C1	121.71 (6)	C14—C9—C8	121.69 (7)
C3—C2—C15	119.83 (6)	C10—C9—C8	119.77 (7)
C1—C2—C15	118.43 (6)	C11—C10—C9	120.71 (7)
C4—C3—C2	118.70 (6)	C11—C10—H10	119.6 (8)
C4—C3—H3	120.7 (7)	C9—C10—H10	119.6 (8)
C2—C3—H3	120.6 (7)	C10—C11—C12	120.12 (7)
C3—C4—C5	121.31 (7)	C10—C11—H11	119.1 (8)
C3—C4—N4	119.36 (6)	C12—C11—H11	120.8 (8)
C5—C4—N4	119.32 (6)	C13—C12—C11	119.89 (7)
C6—C5—C4	119.78 (7)	C13—C12—H12	120.6 (8)
C6—C5—H5	119.1 (7)	C11—C12—H12	119.5 (8)
C4—C5—H5	121.1 (7)	C12—C13—C14	119.67 (7)
C5—C6—C1	121.44 (7)	C12—C13—H13	120.3 (8)
C5—C6—H6	119.1 (8)	C14—C13—H13	120.0 (8)

C1—C6—H6	119.5 (8)	C13—C14—C9	121.07 (7)
N1—C7—C8	112.82 (6)	C13—C14—H14	119.1 (7)
N1—C7—H7A	110.5 (7)	C9—C14—H14	119.8 (7)
C8—C7—H7A	110.5 (7)	N2—C15—C2	177.02 (8)
N1—C7—H7B	105.4 (7)		

C7—N1—C1—C6	1.06 (11)	C4—C5—C6—C1	−0.14 (11)
C7—N1—C1—C2	−178.63 (6)	N1—C1—C6—C5	−178.37 (7)
N1—C1—C2—C3	178.00 (7)	C2—C1—C6—C5	1.33 (11)
C6—C1—C2—C3	−1.70 (10)	C1—N1—C7—C8	−81.27 (9)
N1—C1—C2—C15	−0.18 (10)	N1—C7—C8—C9	−171.53 (6)
C6—C1—C2—C15	−179.88 (6)	C7—C8—C9—C14	−98.73 (8)
C1—C2—C3—C4	0.87 (10)	C7—C8—C9—C10	80.25 (9)
C15—C2—C3—C4	179.03 (6)	C14—C9—C10—C11	−0.20 (11)
C2—C3—C4—C5	0.39 (11)	C8—C9—C10—C11	−179.21 (7)
C2—C3—C4—N4	179.54 (6)	C9—C10—C11—C12	0.90 (11)
O42—N4—C4—C3	3.91 (10)	C10—C11—C12—C13	−0.82 (11)
O41—N4—C4—C3	−176.58 (7)	C11—C12—C13—C14	0.06 (12)
O42—N4—C4—C5	−176.93 (7)	C12—C13—C14—C9	0.65 (12)
O41—N4—C4—C5	2.58 (10)	C10—C9—C14—C13	−0.58 (11)
C3—C4—C5—C6	−0.76 (11)	C8—C9—C14—C13	178.41 (7)
N4—C4—C5—C6	−179.91 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···N2^{i}	0.866 (15)	2.300 (15)	3.0287 (10)	141.9 (12)

Symmetry code: (i) −*x*+1, −*y*, −*z*+2.

(C15H16N2O4S) 4-(methylsulfonyl)-2-nitro-*N*-(2-phenylethyl)aniline

Crystal data

$C_{15}H_{16}N_2O_4S$	D_x = 1.412 Mg m^{-3}
M_r = 320.36	Melting point: 414 K
Tetragonal, $I4_1/a$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -I 4ad	Cell parameters from 53474 reflections
a = 20.4639 (13) Å	θ = 2.6–32.9°
c = 14.3952 (14) Å	μ = 0.24 mm^{-1}
V = 6028.3 (10) Å^3	T = 100 K
Z = 16	Cuboid, yellow
F(000) = 2688	0.40 × 0.20 × 0.20 mm

Data collection

Bruker APEX DUO CCD area-detector diffractometer	52424 measured reflections
	5524 independent reflections
Radiation source: sealed tube	5155 reflections with $I > 2\sigma(I)$
Graphite monochromator	R_{int} = 0.018
ω scans	θ_{max} = 32.9°, θ_{min} = 1.7°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	h = −30→31
	k = −31→30
T_{min} = 0.912, T_{max} = 0.955	l = −21→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.086$
$S = 1.06$
5524 reflections
263 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 3.0117P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.918999 (8)	0.384073 (8)	0.115221 (13)	0.01486 (5)
O21	0.72956 (3)	0.62358 (3)	0.13034 (5)	0.02619 (14)
O22	0.83430 (3)	0.61924 (3)	0.15113 (5)	0.02251 (12)
O41	0.91451 (3)	0.33599 (3)	0.04188 (4)	0.02179 (12)
O42	0.96848 (3)	0.43425 (3)	0.10731 (5)	0.02180 (12)
N1	0.66040 (3)	0.51537 (3)	0.11584 (5)	0.01679 (12)
H1	0.6604 (7)	0.5584 (8)	0.1202 (10)	0.038 (4)*
N2	0.78132 (3)	0.59202 (3)	0.13760 (5)	0.01652 (11)
C1	0.71927 (3)	0.48639 (3)	0.12182 (5)	0.01391 (12)
C2	0.77942 (3)	0.52165 (3)	0.13051 (5)	0.01370 (12)
C3	0.84001 (3)	0.49002 (3)	0.13130 (5)	0.01447 (12)
H3	0.8791 (7)	0.5168 (6)	0.1359 (9)	0.026 (3)*
C4	0.84249 (3)	0.42282 (3)	0.12432 (5)	0.01465 (12)
C5	0.78421 (4)	0.38584 (4)	0.11955 (5)	0.01666 (13)
H5	0.7859 (6)	0.3384 (6)	0.1168 (8)	0.023 (3)*
C6	0.72458 (4)	0.41678 (4)	0.11892 (5)	0.01637 (13)
H6	0.6879 (6)	0.3928 (6)	0.1145 (9)	0.023 (3)*
C7	0.59791 (4)	0.48089 (4)	0.11108 (5)	0.01798 (13)
H7A	0.5906 (5)	0.4561 (5)	0.1693 (8)	0.015 (2)*
H7B	0.5982 (6)	0.4507 (6)	0.0597 (8)	0.018 (3)*
C8	0.54312 (4)	0.53117 (4)	0.09737 (5)	0.01863 (13)
H8A	0.5029 (6)	0.5080 (6)	0.0915 (9)	0.021 (3)*
H8B	0.5525 (6)	0.5542 (6)	0.0391 (9)	0.025 (3)*
C9	0.53881 (3)	0.57928 (4)	0.17680 (5)	0.01547 (12)
C10	0.56452 (4)	0.64241 (4)	0.17008 (5)	0.01871 (13)
H10	0.5853 (6)	0.6565 (7)	0.1136 (9)	0.026 (3)*

C11	0.56197 (4)	0.68488 (4)	0.24613 (6)	0.02200 (15)
H11	0.5775 (6)	0.7276 (7)	0.2407 (10)	0.029 (3)*
C12	0.53446 (4)	0.66439 (4)	0.32954 (6)	0.02297 (15)
H12	0.5339 (7)	0.6937 (7)	0.3812 (10)	0.034 (4)*
C13	0.50872 (4)	0.60148 (4)	0.33686 (5)	0.02155 (14)
H13	0.4898 (7)	0.5856 (7)	0.3950 (10)	0.031 (3)*
C14	0.51036 (4)	0.55957 (4)	0.26071 (5)	0.01777 (13)
H14	0.4927 (6)	0.5155 (6)	0.2656 (9)	0.022 (3)*
C15	0.92951 (4)	0.34181 (4)	0.22080 (6)	0.02208 (14)
H15A	0.9299 (6)	0.3726 (7)	0.2701 (10)	0.031 (3)*
H15B	0.8929 (7)	0.3095 (7)	0.2271 (10)	0.034 (3)*
H15C	0.9713 (7)	0.3212 (7)	0.2172 (10)	0.037 (4)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01361 (8)	0.01350 (8)	0.01747 (9)	0.00014 (5)	0.00355 (5)	−0.00138 (5)
O21	0.0209 (3)	0.0141 (2)	0.0435 (4)	0.0033 (2)	−0.0035 (2)	−0.0016 (2)
O22	0.0192 (3)	0.0156 (2)	0.0328 (3)	−0.00497 (19)	0.0030 (2)	−0.0024 (2)
O41	0.0247 (3)	0.0191 (2)	0.0216 (3)	0.0014 (2)	0.0052 (2)	−0.0065 (2)
O42	0.0150 (2)	0.0172 (2)	0.0332 (3)	−0.00241 (19)	0.0043 (2)	−0.0003 (2)
N1	0.0135 (3)	0.0149 (3)	0.0220 (3)	0.0003 (2)	−0.0005 (2)	−0.0027 (2)
N2	0.0184 (3)	0.0123 (2)	0.0188 (3)	−0.0008 (2)	0.0017 (2)	−0.0005 (2)
C1	0.0138 (3)	0.0140 (3)	0.0140 (3)	−0.0006 (2)	0.0006 (2)	−0.0017 (2)
C2	0.0149 (3)	0.0105 (3)	0.0156 (3)	−0.0010 (2)	0.0010 (2)	−0.0012 (2)
C3	0.0142 (3)	0.0135 (3)	0.0157 (3)	−0.0011 (2)	0.0011 (2)	−0.0015 (2)
C4	0.0138 (3)	0.0128 (3)	0.0173 (3)	−0.0002 (2)	0.0014 (2)	−0.0016 (2)
C5	0.0159 (3)	0.0131 (3)	0.0210 (3)	−0.0010 (2)	0.0007 (2)	−0.0022 (2)
C6	0.0148 (3)	0.0133 (3)	0.0210 (3)	−0.0019 (2)	0.0006 (2)	−0.0024 (2)
C7	0.0140 (3)	0.0191 (3)	0.0209 (3)	−0.0016 (2)	0.0003 (2)	−0.0048 (2)
C8	0.0142 (3)	0.0259 (3)	0.0159 (3)	0.0013 (2)	−0.0016 (2)	−0.0044 (3)
C9	0.0116 (3)	0.0203 (3)	0.0145 (3)	0.0027 (2)	−0.0010 (2)	−0.0006 (2)
C10	0.0176 (3)	0.0209 (3)	0.0176 (3)	0.0014 (2)	−0.0006 (2)	0.0027 (2)
C11	0.0242 (3)	0.0178 (3)	0.0240 (4)	0.0021 (3)	−0.0030 (3)	0.0002 (3)
C12	0.0270 (4)	0.0221 (3)	0.0198 (3)	0.0072 (3)	−0.0021 (3)	−0.0044 (3)
C13	0.0225 (3)	0.0256 (4)	0.0166 (3)	0.0053 (3)	0.0033 (3)	−0.0006 (3)
C14	0.0155 (3)	0.0202 (3)	0.0175 (3)	0.0018 (2)	0.0020 (2)	0.0002 (2)
C15	0.0201 (3)	0.0257 (4)	0.0205 (3)	0.0041 (3)	0.0026 (3)	0.0032 (3)

Geometric parameters (Å, º)

S1—O41	1.4462 (6)	C7—H7A	0.992 (11)
S1—O42	1.4467 (6)	C7—H7B	0.964 (12)
S1—C4	1.7599 (7)	C8—C9	1.5114 (10)
S1—C15	1.7619 (8)	C8—H8A	0.954 (12)
O21—N2	1.2449 (9)	C8—H8B	0.982 (13)
O22—N2	1.2345 (9)	C9—C10	1.3983 (11)
N1—C1	1.3454 (9)	C9—C14	1.4002 (10)
N1—C7	1.4623 (10)	C10—C11	1.3989 (11)
N1—H1	0.882 (16)	C10—H10	0.962 (13)

N2—C2	1.4441 (9)	C11—C12	1.3909 (12)
C1—C6	1.4293 (10)	C11—H11	0.934 (13)
C1—C2	1.4322 (10)	C12—C13	1.3949 (12)
C2—C3	1.3989 (10)	C12—H12	0.955 (14)
C3—C4	1.3797 (10)	C13—C14	1.3922 (11)
C3—H3	0.973 (14)	C13—H13	0.977 (14)
C4—C5	1.4142 (10)	C14—H14	0.974 (12)
C5—C6	1.3746 (10)	C15—H15A	0.949 (14)
C5—H5	0.972 (13)	C15—H15B	1.003 (14)
C6—H6	0.898 (13)	C15—H15C	0.955 (14)
C7—C8	1.5344 (11)		

O41—S1—O42	118.03 (4)	N1—C7—H7B	109.8 (7)
O41—S1—C4	107.72 (4)	C8—C7—H7B	109.6 (7)
O42—S1—C4	107.99 (3)	H7A—C7—H7B	108.8 (10)
O41—S1—C15	107.66 (4)	C9—C8—C7	112.47 (6)
O42—S1—C15	109.33 (4)	C9—C8—H8A	109.9 (7)
C4—S1—C15	105.40 (4)	C7—C8—H8A	108.0 (7)
C1—N1—C7	125.00 (6)	C9—C8—H8B	110.2 (8)
C1—N1—H1	115.8 (10)	C7—C8—H8B	106.9 (7)
C7—N1—H1	118.9 (10)	H8A—C8—H8B	109.3 (10)
O22—N2—O21	121.76 (7)	C10—C9—C14	118.84 (7)
O22—N2—C2	119.00 (6)	C10—C9—C8	121.84 (7)
O21—N2—C2	119.24 (6)	C14—C9—C8	119.29 (7)
N1—C1—C6	120.36 (7)	C9—C10—C11	120.39 (7)
N1—C1—C2	123.58 (7)	C9—C10—H10	120.1 (8)
C6—C1—C2	116.06 (6)	C11—C10—H10	119.4 (8)
C3—C2—C1	121.96 (6)	C12—C11—C10	120.22 (8)
C3—C2—N2	115.91 (6)	C12—C11—H11	119.5 (8)
C1—C2—N2	122.12 (6)	C10—C11—H11	120.3 (9)
C4—C3—C2	119.55 (6)	C11—C12—C13	119.76 (7)
C4—C3—H3	122.5 (8)	C11—C12—H12	119.2 (9)
C2—C3—H3	117.9 (8)	C13—C12—H12	121.0 (9)
C3—C4—C5	120.39 (7)	C14—C13—C12	120.00 (7)
C3—C4—S1	119.15 (5)	C14—C13—H13	118.6 (8)
C5—C4—S1	120.37 (5)	C12—C13—H13	121.4 (8)
C6—C5—C4	120.17 (7)	C13—C14—C9	120.78 (7)
C6—C5—H5	119.5 (8)	C13—C14—H14	120.3 (7)
C4—C5—H5	120.4 (8)	C9—C14—H14	118.9 (7)
C5—C6—C1	121.75 (7)	S1—C15—H15A	108.7 (8)
C5—C6—H6	119.4 (8)	S1—C15—H15B	108.1 (8)
C1—C6—H6	118.9 (8)	H15A—C15—H15B	112.0 (11)
N1—C7—C8	108.76 (6)	S1—C15—H15C	106.2 (9)
N1—C7—H7A	109.9 (6)	H15A—C15—H15C	109.1 (12)
C8—C7—H7A	110.0 (6)	H15B—C15—H15C	112.6 (12)

C7—N1—C1—C6	3.38 (11)	C15—S1—C4—C5	−72.35 (7)
C7—N1—C1—C2	−177.13 (7)	C3—C4—C5—C6	2.03 (11)
N1—C1—C2—C3	−176.34 (7)	S1—C4—C5—C6	−174.59 (6)

C6—C1—C2—C3	3.18 (10)	C4—C5—C6—C1	0.80 (11)
N1—C1—C2—N2	2.73 (11)	N1—C1—C6—C5	176.24 (7)
C6—C1—C2—N2	−177.76 (6)	C2—C1—C6—C5	−3.29 (10)
O22—N2—C2—C3	−5.65 (10)	C1—N1—C7—C8	−175.70 (7)
O21—N2—C2—C3	174.68 (7)	N1—C7—C8—C9	−61.20 (8)
O22—N2—C2—C1	175.24 (7)	C7—C8—C9—C10	101.15 (8)
O21—N2—C2—C1	−4.44 (10)	C7—C8—C9—C14	−76.55 (8)
C1—C2—C3—C4	−0.55 (10)	C14—C9—C10—C11	0.21 (11)
N2—C2—C3—C4	−179.66 (6)	C8—C9—C10—C11	−177.50 (7)
C2—C3—C4—C5	−2.14 (10)	C9—C10—C11—C12	0.74 (12)
C2—C3—C4—S1	174.53 (5)	C10—C11—C12—C13	−0.70 (12)
O41—S1—C4—C3	−134.28 (6)	C11—C12—C13—C14	−0.30 (12)
O42—S1—C4—C3	−5.78 (7)	C12—C13—C14—C9	1.27 (12)
C15—S1—C4—C3	110.98 (6)	C10—C9—C14—C13	−1.21 (11)
O41—S1—C4—C5	42.39 (7)	C8—C9—C14—C13	176.56 (7)
O42—S1—C4—C5	170.88 (6)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.882 (16)	1.951 (16)	2.6364 (9)	133.4 (14)