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Unexpected beauty and diversity in the structures of three homologous 4,5-dialkoxy-1-ethynyl-2-nitrobenzenes: the subtle interplay between intermolecular C—H···O hydrogen bonds and alkyl chain length

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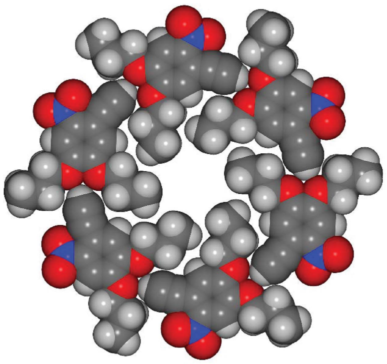
The synthesis, ^{1}H and ^{13}C NMR spectra, and X-ray structures are described for three dialkoxy ethynylnitrobenzenes that differ only in the length of the alkoxy chain, namely 1-ethynyl-2-nitro-4,5-dipropoxybenzene, $C_{14}H_{17}NO_4$, 1,2-dibutoxy-4-ethynyl-5-nitrobenzene, $C_{16}H_{21}NO_4$, and 1-ethynyl-2-nitro-4,5-dipentoxybenzene, $C_{18}H_{25}NO_4$. Despite the subtle changes in molecular structure, the crystal structures of the three compounds display great diversity. Thus, 1-ethynyl-2-nitro-4,5-dipropoxybenzene crystallizes in the trigonal crystal system in the space group $R\overline{3}$, with $Z = 18$, 1,2-dibutoxy-4-ethynyl-5-nitrobenzene crystallizes in the monoclinic crystal system in the space group $P2_1/c$, with $Z = 4$, and 1-ethynyl-2-nitro-4,5-dipentoxybenzene crystallizes in the triclinic crystal system in the space group $P\overline{1}$, with $Z = 2$. The crystal structure of 1-ethynyl-2-nitro-4,5-dipropoxybenzene is dominated by planar hexamers formed by a bifurcated alkoxy *sp*-C—H···O,O′ interaction, while the structure of the dibutoxy analogue is dominated by planar ribbons of molecules linked by a similar bifurcated alkoxy *sp*-C—H···O,O′ interaction. In contrast, the dipentoxy analogue forms ribbons of molecules alternately connected by a self-complementary *sp*-C—H···O_2N interaction and a self-complementary sp^2-C—H···O_2N interaction. Disordered solvent was included in the crystals of 1-ethynyl-2-nitro-4,5-dipropoxybenzene and its contribution was removed during refinement.

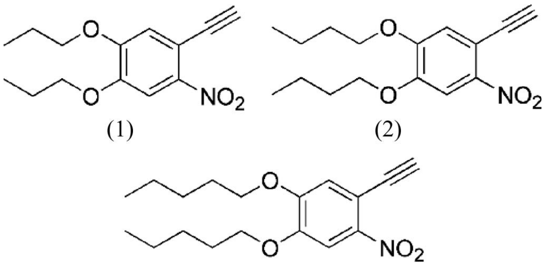
1. Introduction

The role of weak interactions between organic molecules, including nonconventional C—H···O hydrogen bonds, has long been recognized in solid-state structures (Sutor, 1962, 1963). Indeed, extensive reviews were published two decades ago (Desiraju & Steiner, 1999; Alkorta & Elguero, 1998). More recently, the importance of C—H···O hydrogen bonds in protein ligand-binding sites has been identified (Panigrahi & Desiraju, 2007) and related to the stability of enzymes (Lavanya *et al.*, 2013). Also, studies support the incorporation of the role of C—H···O hydrogen bonds in kinase inhibitor design (Panigrahi, 2008) and structure-based drug design (Desiraju, 2005).

While the importance of a particular interaction in a crystal structure is often difficult to assign, it is accepted that in some instances weak interactions, such as C—H···O hydrogen bonds, may be considered structure determining. Indeed, our first studies were aimed at demonstrating the importance and control of nonconventional hydrogen bonding in cocrystallization (Bosch, 2010, 2014). In that study, we demonstrated that



the *sp*-C—H···N hydrogen bond between dipyridines and diethynylbenzenes controlled the formation of cocrystals. In contrast, the *sp*-C—H···O(carbonyl) hydrogen-bonding interaction was less efficient, in our hands, as a driving force for cocrystallization of different molecules which was significantly less predictable (Bosch, 2016). In a separate study, we investigated the structure of two *ortho*-nitrophenylacetylenes and observed unusual C—H···O interactions (Bosch & Jeffries, 2016), so we decided to further investigate C—H···O_2N interactions in three 4,5-dialkoxy-1-ethynyl-2-nitrobenzenes, namely 1-ethynyl-2-nitro-4,5-dipropoxybenzene, (1), 1,2-dibutoxy-4-ethynyl-5-nitrobenzene, (2), and 1-ethynyl-2-nitro-4,5-dipentoxybenzene, (3) (see Scheme).



(1) (2)

(3)

2. Experimental

2.1. Synthesis and characterization

The Williamson ether synthesis was used to prepare each of 1,2-dipropoxybenzene, 1,2-dibutoxybenzene, and 1,2-dipentoxybenzene from catechol, 2.2 equivalents of KOH and 2.5 equivalents of the corresponding 1-bromoalkane in acetone. Each of these compounds was then iodinated using mercuric iodide and iodine (Bacher *et al.*, 1999) to form the corresponding 1,2-dialkoxy-4-iodobenzene. The resultant dialkoxyiodobenzenes were nitrated with nitric acid in acetic acid and then subjected to Sonogashira cross-coupling with trimethylsilylacetylene. Finally, base-promoted deprotection provided the dialkoxyethynylnitrobenzenes. The full procedure is given for the dipropoxy derivative.

2.1.1. 1-Iodo-2-nitro-4,5-dipropoxybenzene. 1-Iodo-3,4-dipropoxybenzene (1.96 g, 6.12 mmol) was dissolved in glacial acetic acid (4 ml) and the mixture cooled to 273 K. A mixture of nitric acid (1 ml, 24 mmol) and acetic acid (1.3 ml) was then added dropwise to the reaction mixture, which was stirred at 273 K for 40 min. The reaction mixture was dissolved in dichloromethane (100 ml) and washed twice with water (100 ml), and then 5% aqueous sodium bicarbonate (75 ml). The dichloromethane solution was dried over magnesium sulfate and the solvent evaporated. The crude solid was recrystallized from a propan-2-ol/water mixture (100 ml, 9:1 *v*/*v*) as thin yellow needles (yield 0.89 g, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (*s*, 1H), 7.37 (*s*, 1H), 4.02 (*m*, 4H), 1.87 (*m*, 4H), 1.06 (*m*, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.97, 148.83, 124.30, 110.51, 71.09, 70.93, 22.27, 13.74.

2.1.2. 1-Ethynyl-2-nitro-4,5-dipropoxybenzene, (1). A mixture of 1-iodo-2-nitro-4,5-dipropoxybenzene (0.88 g, 2.4 mmol), bis(triphenylphosphane)palladium(II) chloride (73 mg, 0.103 mmol), and copper(I) iodide (6.8 mg, 0.03 mmol) in triethylamine (12 ml) was stirred under an argon atmosphere for 3 min. Trimethylsilylacetylene (0.414 g, 0.6 ml, 4.2 mmol) was added, the flask sealed, and the reaction mixture stirred under an inert atmosphere for 24 h at 298 K. The reaction mixture was added to dichloromethane (150 ml), washed four times with water (50 ml), dried over magnesium sulfate, and the solvent evaporated to yield a dark-brown crude product. This crude product was purified using flash chromatography to give trimethyl-(2-nitro-4,5-dipropoxyphenylethynyl)silane as an off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (*s*, 1H), 6.98 (*s*, 1H), 4.03 (*q*, *J* = 8.0 Hz, 4H), 1.87 (*m*, 4H), 1.04 (*m*, 6H), 0.26 (*s*, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.94, 149.06, 143.21, 124.32, 110.49, 105.00, 69.41, 69.24, 19.06, 19.08, 13.72, 0.00. Trimethyl(2-nitro-4,5-dipropoxyphenylethynyl)silane was deprotected using sodium hydroxide in methanol to give (1) as a light-brown solid. The product was purified using flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (*s*, 1H), 7.02 (*s*, 1H), 4.04 (*t*, *J* = 6 Hz, 4H), 3.46 (*s*, 1H), 1.93–1.84 (*m*, 4H), 1.07 (*t*, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.72, 149.03, 142.936, 117.17, 110.97, 108.77, 83.28, 79.54, 70.87, 22.19, 22.18, 10.26, 10.25.

2.1.3. 1,2-Dibutoxy-4-iodo-5-nitrobenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (*s*, 1H), 7.37 (*s*, 1H), 4.06 (*t*, *J* = 7 Hz, 2H), 4.04 (*t*, *J* = 7 Hz, 2H), 1.84 (*m*, 4H), 1.51 (*m*, 4H), 1.00 (*t*, *J* = 8 Hz, 3H), 0.99 (*t*, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.19, 149.05, 144.90, 124.46, 110.67, 69.61, 69.43, 31.06, 31.04, 19.30, 19.28, 13.97, 13.95.

2.1.4. 1,2-Dibutoxy-4-ethynyl-5-nitrobenzene (2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (*s*, 1H), 7.02 (*s*, 1H), 4.08 (*t*, *J* = 6 Hz, 4H), 3.45 (*s*, 1H), 1.87–1.80 (*m*, 4H), 1.50 (sextet, *J* = 6 Hz, 4H), 0.98 (*t*, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.00, 149.33, 143.23, 127.39, 110.23, 109.01, 83.50, 79.83, 69.47, 69.45, 32.03, 19.30, 19.28, 13.96, 13.94.

2.1.5. 1-Iodo-2-nitro-4,5-dipentoxybenzene. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (*s*, 1H), 7.37 (*s*, 1H), 4.05 (*t*, *J* = 7 Hz, 2H), 4.03 (*t*, *J* = 7 Hz, 2H), 1.84 (*m*, 4H), 1.44 (*m*, 8H), 0.94 (*t*, *J* = 7 Hz, 3H), 0.93 (*t*, *J* = 7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.17, 149.03, 144.90, 124.43, 110.64, 69.89, 69.70, 28.72, 28.70, 28.24, 28.21, 22.55, 22.53, 14.17.

2.1.6. 1-Ethynyl-2-nitro-4,5-dipentoxybenzene, (3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (*s*, 1H), 7.02 (*s*, 1H), 4.07 (*t*, *J* = 7 Hz, 4H), 3.46 (*s*, 1H), 1.86 (quintet, *J* = 7 Hz, 4H), 1.51–1.36 (*m*, 8H), 0.94 (*t*, *J* = 7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.96, 149.28, 143.18, 117.33, 111.20, 108.95, 83.52, 79.81, 69.72, 69.69, 28.68, 28.67, 28.22, 28.21, 22.52, 22.51, 14.13.

2.2. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 1. The phenyl and alkynyl H atoms involved in C—H···O hydrogen bonds were refined with distance restraints of C—H = 0.93 (2) (phenyl) and 0.95 (2) Å (alkynyl), and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The methylene, methyl, and remaining phenyl H atoms were treated as riding in geometrically idealized positions, with

Table 1
Experimental details.

Experiments were carried out at 100 K with Mo $K\alpha$ radiation using a Bruker APEXII CCD diffractometer. Absorption was corrected for by multi-scan methods (*SADABS*; Bruker, 2014).

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{14}H_{17}NO_4$	$C_{16}H_{21}NO_4$	$C_{18}H_{25}NO_4$
M_r	263.29	291.34	319.39
Crystal system, space group	Trigonal, $R\overline{3}$	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
a, b, c (Å)	26.6774 (16), 26.6774 (16), 10.3451 (6)	8.5209 (5), 18.0914 (10), 9.9579 (5)	4.570 (4), 9.415 (8), 20.968 (18)
α, β, γ (°)	90, 90, 120	90, 97.967 (1), 90	94.003 (12), 90.758 (12), 93.435 (11)
V (Å^3)	6376.1 (8)	1520.24 (14)	898.2 (14)
Z	18	4	2
μ (mm^{-1})	0.09	0.09	0.08
Crystal size (mm)	0.07 × 0.07 × 0.04	0.60 × 0.34 × 0.02	0.46 × 0.14 × 0.14
Data collection			
$T_{\min}$, $T_{\max}$	0.697, 0.746	0.682, 0.746	0.382, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	28334, 3172, 2420	19579, 3370, 2449	5380, 2914, 1604
$R_{\rm int}$	0.039	0.047	0.055
$(\sin \theta/\lambda)_{\max}$ (Å^{-1})	0.643	0.643	0.581
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.138, 1.06	0.041, 0.103, 1.02	0.085, 0.262, 1.03
No. of reflections	3172	3370	2914
No. of parameters	180	198	216
No. of restraints	2	2	2
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.43, −0.20	0.25, −0.18	0.36, −0.32

Computer programs: *SMART* (Bruker, 2014), *SAINT* (Bruker, 2014), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *X-SEED* (Barbour, 2001).

C—H = 0.95 (aromatic), 0.99 (methylene), or 0.96 Å (methyl), and with $U_{\rm iso}({\rm H}) = kU_{\rm eq}({\rm C})$, where $k = 1.5$ for the methyl group and 1.2 for the phenyl and methylene groups.

In the refinement of (1), the routine SQUEEZE (Spek, 2015) in *PLATON* (Spek, 2009) was used to calculate the voids within which disordered solvent molecules were found, and the refinement was completed without these disordered solvent residues. Three voids of almost equivalent volume (115, 115, and 125 Å^3) were identified with an electron count of 38 electrons each. These reasonably correspond to dichloromethane molecules with electron counts of 42 electrons.

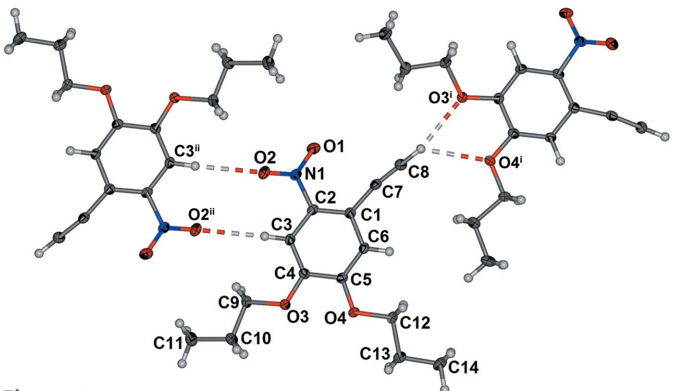


Figure 1
The labelled asymmetric unit of (1), showing the bifurcated *sp*-C—H···O(nitro) hydrogen bond and the self-complementary phenyl *sp*^{2}-C—H···O(nitro) hydrogen bond. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$; (ii) $-x + \frac{4}{3}, -y + \frac{5}{3}, -z + \frac{2}{3}$.]

Compound (3) crystallized as fragile thin needle-like rods. Data were collected from multiple crystals, all of which resulted in the same unit cell from weak data. The structure was thus refined using only data to a resolution limit of 0.86 Å. The *R* factor is accordingly significantly higher for (3) than for (1) or (2). The possibility of an incorrectly assigned space group or twinning were discounted after evaluation using the routines ADDSYM and TWINROTMAT with the *PLATON* (Spek, 2009) interface.

3. Results and discussion

Compound (1) crystallizes from dichloromethane in the trigonal space group $R\overline{3}$ with one molecule in the asymmetric unit (Fig. 1). The molecule is essentially planar, with most non-H atoms within 0.1 Å of the plane defined by the C1–C6 benzene ring. The nitro group is twisted by about 18° with respect to the benzene ring, with torsion angles C3—C2—N1—O2 = 17.89 (17)° and C1—C2—N1—O1 = 18.77 (18)°. Consequently, atom O2 is 0.339 (4) Å above the plane of the benzene ring and atom O1 is 0.343 (5) Å below this plane. The ethynyl group is slightly bent to accommodate the bulk of the adjacent nitro group, with a C1—C7—C8 angle of 170.34 (13)°. One propoxy chain is slightly below the plane of the benzene ring, with atoms C9 and C11 distances of 0.155 (5) and 0.320 (7) Å, respectively, below the plane of the benzene ring. The two major intermolecular interactions are both nonconventional hydrogen bonds. One of these is an asymmetric bifurcated *sp*-C—H···O hydrogen bond, as shown in Fig. 1 and Table 2. The C···O distances C8···O3$^{\rm i}$ and

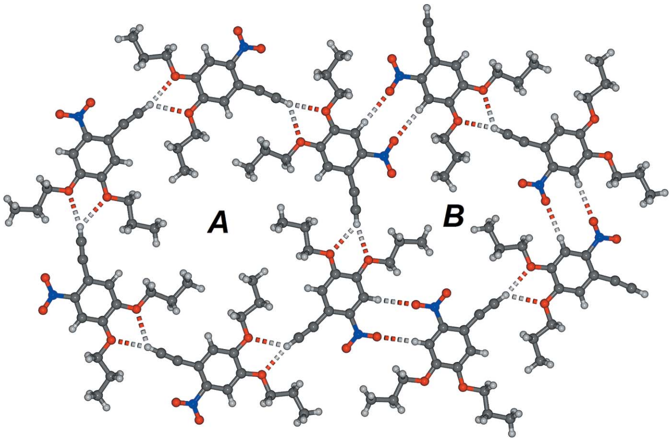


Figure 2
A view of the nonconventional *sp*-C—H···O hydrogen-bonded hexamer of molecules of (1). In the hexamer on the left-hand side, the six molecules are linked through an asymmetric bifurcated alkoxy *sp*-C—H···O,O′ hydrogen bond to form hexagon *A*, while on the right-hand side the molecules are alternately linked through a bifurcated alkoxy *sp*-C—H···O,O′ hydrogen bond and a self-complementary sp^2-C—H···O hydrogen bond, to form hexagon *B*.

C8···O4^{i} are 3.4001 (16) and 3.3267 (16) Å, respectively, with C8—H8···O3^{i} and C8—H8···O4^{i} hydrogen-bond angles of 166.7 (15) and 132.5 (13)°, respectively [symmetry code: (i) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$]. The second intermolecular interaction is a self-complementary nonconventional hydrogen bond between the phenyl group and a nitro O atom,with a C3···O2^{ii} distance of 3.5459 (16) Å, an H3···O2^{ii} distance of 2.611 (14) Å and a C3—H3···O2^{ii} angle of 176.5 (15)° [symmetry code: (ii) $-x + \frac{4}{3}, -y + \frac{5}{3}, -z + \frac{2}{3}$].

The hydrogen-bonded molecules are arranged into bifurcated *sp*-C—H···O hydrogen-bonded hexamers, as shown on the left-hand side of Fig. 2. The propyl group of each molecule is folded into the center of the hexamer, while the nitro group is on the exterior of the hexamer. The exterior nitro group of each molecule forms a self-complementary phenyl–nitro sp^2-C—H···O hydrogen bond to the nitrophenyl group of a molecule in an adjacent hexamer. This results in a secondary hexamer in which six molecules are linked by alternating bifurcated *sp*-C—H···O hydrogen bonds and the self-complementary sp^2-C—H···O hydrogen-bonded assembly shown on the right-hand side of Fig. 2. These hexamers extend to form a planar arrangement, as shown in Fig. 3.

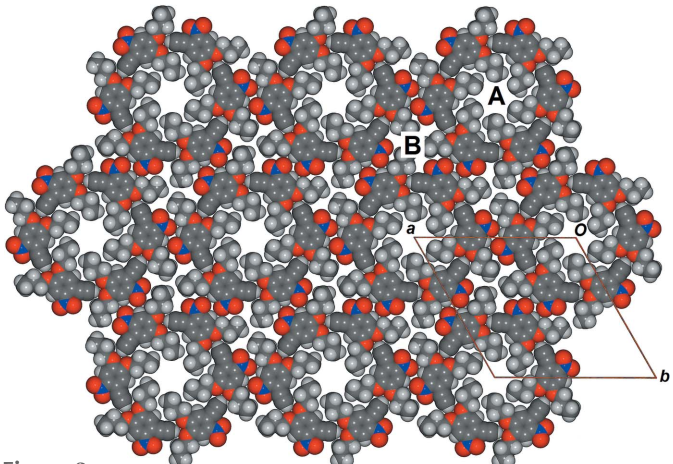


Figure 3
A view, along the *c* axis, of part of the planar sheet of molecules of (1) forming two distinct hydrogen-bonded hexagons *A* and *B*.

Table 2
Selected hydrogen-bond parameters (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
(1)				
C8—H8···O3^{i}	0.935 (9)	2.483 (10)	3.4001 (16)	166.7 (15)
C8—H8···O4^{i}	0.935 (9)	2.623 (15)	3.3267 (16)	132.5 (13)
C3—H3···O2^{ii}	0.936 (14)	2.611 (14)	3.5459 (16)	176.5 (15)
(2)				
C8—H8···O3^{iii}	0.947 (13)	2.609 (14)	3.3835 (19)	139.3 (12)
C8—H8···O4^{iii}	0.947 (13)	2.553 (14)	3.4371 (19)	155.5 (13)
(3)				
C3—H3···O2^{iv}	0.93 (2)	2.88 (3)	3.793 (7)	167 (7)
C9—H9*A*···O2^{iv}	0.99	2.55	3.254 (7)	128
C8—H8···O1^{v}	0.95 (2)	2.45 (3)	3.381 (8)	167 (8)

Symmetry codes: (i) $y + \frac{1}{3}, -x + y + \frac{2}{3}, -z + \frac{2}{3}$; (ii) $-x + \frac{4}{3}, -y + \frac{5}{3}, -z + \frac{2}{3}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x, -y + 1, -z + 1$; (v) $-x + 2, -y, -z + 1$.

Compound (2) crystallizes from dichloromethane in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 4). The structure of the asymmetric unit is similar to that described for (1). The nitro group is less twisted with respect to the benzene ring, with the C3—C2—N1—O2 and C1—C2—N1—O1 torsion angles both equal to 6.1 (2)°. Atom O1 is 0.185 (3) Å above the plane of the benzene ring and atom O2 is 0.037 (2) Å below this plane. The pendant butoxy chains are both planar and the terminal C atoms are 0.039 (3) and 0.032 (3) Å out of the plane defined by the first three atoms in the chains. These methyl C atoms, *i.e.* C12 and C16, are below and above the plane of the benzene ring by 0.604 (5) and 0.503 (5) Å, respectively. The ethynyl group is slightly bent, with a C1—C7—C8 angle of 172.37 (16)°.

The major intermolecular interaction between molecules of (2) is an asymmetric bifurcated *sp*-C—H···O hydrogen bond, shown in Fig. 4. The C···O distances C8···O3^{iii} and C8···O4^{iii}

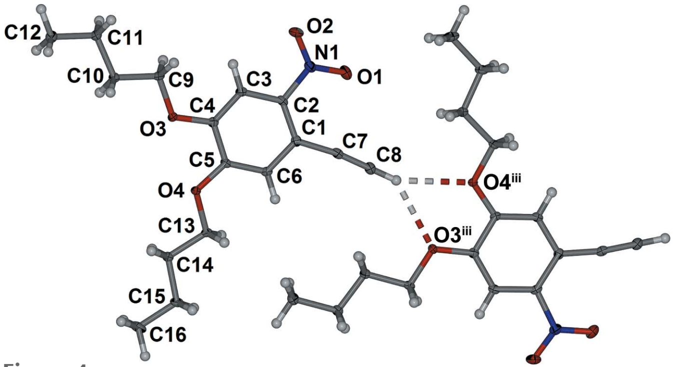


Figure 4
The labeled asymmetric unit of (2), showing the bifurcated alkoxy *sp*-C—H···O,O′ hydrogen bond. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.]

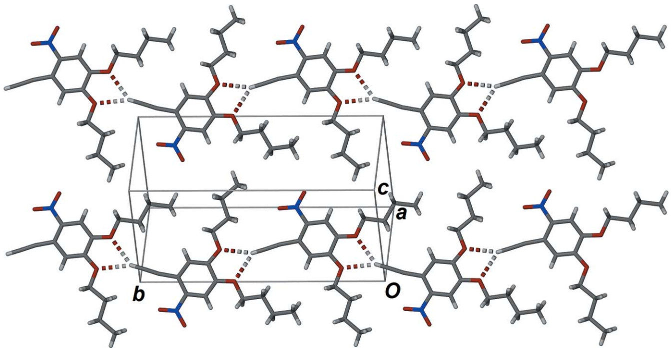


Figure 5
A view of a portion of the two-dimensional sheet formed from three adjacent linear ribbons of *sp*-C—H···O hydrogen-bonded molecules of (2).

are 3.3835 (19) and 3.4371 (19) Å, respectively, with C8—H8···O3^{iii} and C8—H8···O4^{iii} angles of 139.3 (12) and 155.5 (13)°, respectively [symmetry code: (iii) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$]. The major difference from compound (1) is the relative orientation of the ethynyl group in adjacent hydrogen-bonded molecules. The fact that the relative orientations of the ethynyl and nitro groups are flipped in the structure of (2) relative to (1) results in the formation of linear hydrogen-bonded ribbons in (2), shown in Fig. 5, in place of the cyclic hexamers in (1). There is one close contact between one of the methyl H atoms and a nitro O atom. It is reasonable that the longer butoxy side chain is too large to facilitate hydrogen-bonded hexagon formation, as observed with (1).

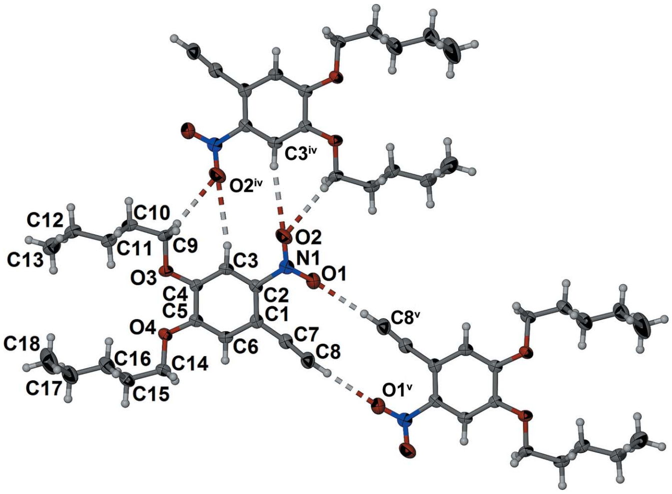


Figure 6
The labeled asymmetric unit of (3), showing the self-complementary alkyne–nitro *sp*-C—H···O hydrogen bond and the self-complementary phenyl–nitro sp^2-C—H···O hydrogen bond. Displacement ellipsoids drawn at the 50% probability level. [Symmetry codes: (iv) $-x$, $-y + 1$, $-z + 1$; (v) $-x + 2$, $-y$, $-z + 1$.]

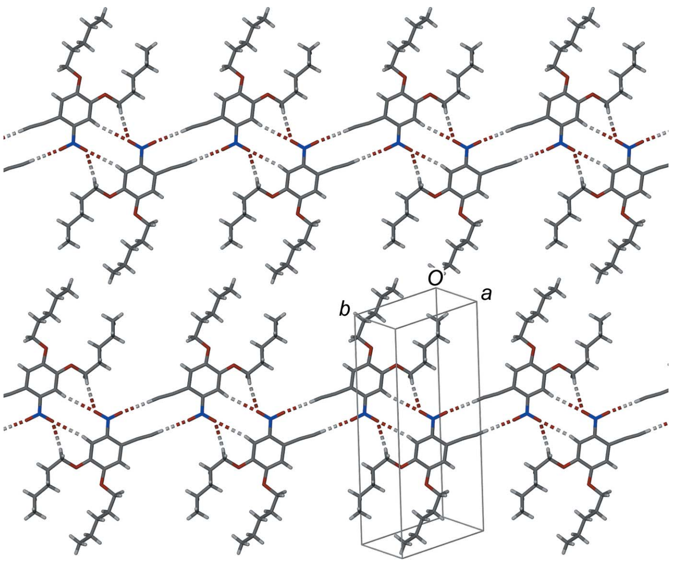


Figure 7
A view of the structure of (3), showing the formation of planar sheets.

Compound (3) crystallizes from dichloromethane in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit (Fig. 6). Similar to the structures of (1) and (2), the nitro group in (3) is also slightly twisted with respect to the benzene ring, with torsion angles C3—C2—N1—O2 and C1—C2—N1—O1 equal to 8.0 (6) and 8.4 (6)°, respectively. Atom O1 is 0.153 (7) Å above the plane of the benzene ring and atom O2 is 0.143 (7) Å below this plane. The ethynyl group is also slightly bent, with a C1—C7—C8 angle of 173.9 (6)°. In contrast with the structures of (1) and (2), the two pentoxy chains are not coplanar with the benzene ring and the terminal methyl C atoms, *i.e.* C13 and C18, are 2.145 (14) and 2.120 (16) Å, respectively, above the plane of the benzene ring. Furthermore, the major intermolecular interaction is a self-complementary *sp*-C—H···O(nitro) hydrogen bond, as shown in Fig. 6. The C···O distance C8···O1^{v} is 3.381 (8) Å, with a C8—H8···O1^{v} angle of 167 (8)° [symmetry code: (v) $-x + 2$, $-y$, $-z + 1$]. There is an sp^2-C—H···O(nitro) self-complementary hydrogen bond between an adjacent benzene H atom and the second nitro O atom (Fig. 6). The C···O distance C3···O2^{iv} is 3.793 (7) Å, with a C3—H3···O2^{iv} angle of 167 (7)° [symmetry code: (iv) $-x$, $-y + 1$, $-z + 1$]. In addition, one nitro O atom has a close contact to the adjacent methylene H atom on C9, with a C9···O2^{iv} distance of 3.254 (7) Å and a C9—H9*A*···O2^{ii} angle of 128°. The *sp*-C—H···O(nitro) interaction binds a pair of molecules together, while the sp^2-C—H···O(nitro) interaction links these hydrogen-bonded dimers together in parallel ribbons, as shown in Fig. 7.

In order to put the interactions observed in these three structures into context, we searched the Cambridge Structural Database (CSD; Version 5.38, updates 1 and 2; Groom *et al.*, 2016) using *Conquest* (Bruno *et al.*, 2002) for each of the three nonconventional hydrogen bonds we have described. These are shown in Fig. 8 as (*a*) the bifurcated alkoxy *sp*-C—H···O,O′ interaction, (*b*) the self-complementary *sp*-C—H···O(nitro) interaction and (*c*) the self-complementary sp^2-C—H···O(nitro) interaction. For each search, the H···O contact was limited to those structures displaying contacts less than or equal to 2.72 Å, the sum of the van der Waals radii (Bondi, 1964).

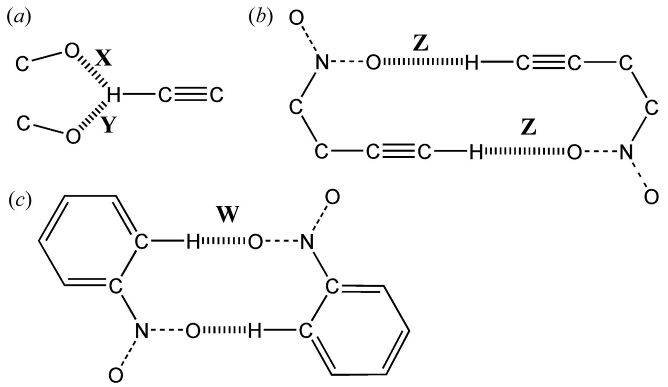


Figure 8
The criteria used for the CSD search for (*a*) the bifurcated *sp*-C—H···O interaction with contacts **X** and **Y**, (*b*) the self-complementary *sp*-C—H···O(nitro) interaction with contact **Z**, and (*c*) the self-complementary phenyl sp^2-C—H···O(nitro) interaction **W**. All contacts are less than or equal to the sum of the van der Waals radii.

For the bifurcated *sp*-C—H···O interaction observed in the structures of (1) and (2), the search criteria were set to find structures with a bifurcated interaction in which both H···O distances are less than or equal to the sum of the van der Waals radii, as shown in Fig. 8(*a*). In addition, the distances between the terminal alkyne C atom and the O atom were recorded, as well as the two C—H···O and two C—O···H angles. A total of 16 examples were found. One example (CSD refcode QIKLOL; Murty & Vasella, 2001) was excluded, since the C—H···O angles of 176.8 and 108.3° suggest that this is really a linear interaction with a second close contact. Interestingly, the particularly short reported distance of 2.065 Å in this structure corresponds to an unreasonably long C—H distance of 1.176 Å. The H···O distances in the remaining 15 structures ranged from 2.267 Å (corresponding to 83.3% of the sum of van der Waals radii) to the sum of the van der Waals radii. 10 of these 15 are structures of single relatively small organic molecules that contain multiple O atoms and at least one terminal alkyne and no other significant intermolecular interactions. Three structures also include conventional hydrogen bonds and two structures are coordination complexes that include a terminal alkyne group and multiple O atoms. It is noteworthy that there is a single example of a trifurcated *sp*-C—H···O(trialkoxy) interaction (refcode QELFES; Paquette *et al.*, 2000). In future, we plan to explore the application of the rare bifurcated *sp*-C—H···O interaction to the cocrystallization of different molecules in the absence of stronger intermolecular interactions.

For the self-complementary *sp*-C—H···O(nitro) interaction observed in structure (3), the CSD search criteria were set to find structures with alkyne–nitro H···O distances less than or equal to the sum of the van der Waals radii, as shown in Fig. 8(*b*). Only two structures were found to display this interaction: 4,5-dimethyl-2-nitrophenylacetylene (refcode OSAQIK; Bosch & Jeffries, 2016) and 2-amino-5-nitro-1,4-diethynylbenzene (refcode SOLHUX; Batsanov, 2008). In contrast with these two rare interactions, the self-complementary phenyl C—H···O(nitro) interaction, shown in Fig. 8(*c*), is very common, appearing in 2832 structures, and it can be considered a reliable supramolecular synthon for nitrobenzenes.

4. Conclusions

The X-ray structures of three homologous dialkoxyethynylnitrobenzenes display a variety of three-dimensional structures controlled by C—H···O interactions. The structures are modulated by the alkyl chain length. The self-complementary phenyl C—H···O(nitro) interaction is clearly a reliable synthon that should be considered in the design of supramolecular systems that include nitrobenzenes. Furthermore, we believe that the bifurcated alkyne C—H···O interaction shown in Fig. 8(*a*), while not common, is a synthon that has potential application in supramolecular chemistry.

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Unexpected beauty and diversity in the structures of three homologous 4,5-dialkoxy-1-ethynyl-2-nitrobenzenes: the subtle interplay between intermolecular C—H···O hydrogen bonds and alkyl chain length

Shalisa M. Oburn and Eric Bosch

Computing details

For all structures, data collection: Bruker *SMART*; cell refinement: Bruker *SMART*; data reduction: Bruker *SAINT*; program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2015); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2015a); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED* (Barbour, 2001).

(1)

Crystal data

$C_{14}H_{17}NO_4$
$M_r = 263.29$
Trigonal, $R\bar{3}:H$
$a = 26.6774\ (16)$ Å
$c = 10.3451\ (6)$ Å
$V = 6376.1\ (8)$ Å^3
$Z = 18$
$F(000) = 2520$

$D_x = 1.234$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5437 reflections
$\theta = 2.6$–$27.1°$
$\mu = 0.09$ mm^{-1}
$T = 100$ K
Cut rectangular prism, colourless
0.07 × 0.07 × 0.04 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS Version 2014; Bruker AXS)
$T_{min} = 0.697$, $T_{max} = 0.746$

28334 measured reflections
3172 independent reflections
2420 reflections with $I > 2\sigma(I)$
$R_{int} = 0.039$
$\theta_{max} = 27.2°$, $\theta_{min} = 1.5°$
$h = -34 \rightarrow 34$
$k = -34 \rightarrow 34$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.138$
$S = 1.06$
3172 reflections
180 parameters
2 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2 + 1.9773P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

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

Refinement. # SQUEEZE RESULTS # Note: Data are Listed for all Voids in the P1 Unit Cell # i.e. Centre of Gravity, Solvent Accessible Volume, # Recovered number of Electrons in the Void and # Details about the Squeezed Material loop_ _platon_squeeze_void_nr _platon_squeeze_void_average_x _platon_squeeze_void_average_y _platon_squeeze_void_average_z _platon_squeeze_void_volume _platon_squeeze_void_count_electrons _platon_squeeze_void_content 1 0.000 0.000 0.000 125 38 ′ ′ 2 0.333 0.667 0.667 115 38 ′ ′ 3 0.667 0.333 0.333 115 38 ′ ′

_platon_squeeze_details ′Reasonable that the squeezed solvent corresponds to dichloromethane (42 e)′

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.80137 (4)	0.82653 (4)	0.29721 (12)	0.0429 (3)
N1	0.75096 (5)	0.80819 (5)	0.32978 (11)	0.0256 (3)
C1	0.73231 (5)	0.70715 (5)	0.33025 (12)	0.0206 (3)
O2	0.73202 (4)	0.83983 (4)	0.36150 (11)	0.0375 (3)
C2	0.71127 (5)	0.74567 (5)	0.32948 (12)	0.0212 (3)
O3	0.55388 (4)	0.64527 (4)	0.32599 (9)	0.0261 (2)
C3	0.65221 (6)	0.72722 (5)	0.32879 (12)	0.0212 (3)
O4	0.59014 (4)	0.57189 (4)	0.32933 (9)	0.0244 (2)
C4	0.61230 (5)	0.66862 (5)	0.32747 (12)	0.0209 (3)
C5	0.63200 (5)	0.62827 (5)	0.32965 (12)	0.0209 (3)
C6	0.69061 (5)	0.64767 (5)	0.33122 (12)	0.0205 (3)
H6	0.703270	0.620132	0.333023	0.025*
C7	0.79185 (6)	0.72157 (5)	0.33451 (12)	0.0232 (3)
C8	0.83787 (6)	0.72495 (6)	0.33970 (14)	0.0286 (3)
C9	0.53135 (6)	0.68428 (6)	0.31049 (13)	0.0252 (3)
H9A	0.543558	0.704456	0.226250	0.030*
H9B	0.546036	0.713660	0.380149	0.030*
C10	0.46645 (6)	0.64833 (6)	0.31691 (16)	0.0336 (3)
H10A	0.454772	0.629926	0.403095	0.040*
H10B	0.452595	0.617229	0.251226	0.040*
C11	0.43856 (7)	0.68527 (7)	0.2930 (2)	0.0480 (5)
H11A	0.453678	0.717186	0.355410	0.072*
H11B	0.396514	0.661425	0.303249	0.072*
H11C	0.447534	0.700984	0.205091	0.072*
C12	0.60887 (6)	0.52969 (5)	0.33039 (13)	0.0239 (3)
H12A	0.630358	0.533250	0.411084	0.029*
H12B	0.634935	0.536310	0.256252	0.029*
C13	0.55624 (6)	0.47007 (6)	0.32152 (15)	0.0290 (3)
H13A	0.534786	0.466784	0.240927	0.035*
H13B	0.530215	0.463725	0.395589	0.035*
C14	0.57451 (7)	0.42451 (6)	0.32240 (17)	0.0374 (4)
H14A	0.598579	0.429645	0.246451	0.056*
H14B	0.540037	0.385883	0.320216	0.056*

H14C	0.596699	0.428606	0.401088	0.056*
H3	0.6402 (8)	0.7547 (7)	0.3249 (16)	0.045*
H8	0.8740 (5)	0.7274 (8)	0.3423 (16)	0.045*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0265 (6)	0.0225 (5)	0.0748 (8)	0.0085 (4)	0.0085 (5)	0.0029 (5)
N1	0.0259 (6)	0.0183 (6)	0.0312 (6)	0.0101 (5)	−0.0031 (5)	−0.0002 (4)
C1	0.0218 (6)	0.0205 (6)	0.0188 (6)	0.0101 (5)	−0.0019 (5)	−0.0009 (5)
O2	0.0337 (6)	0.0217 (5)	0.0597 (7)	0.0158 (4)	−0.0025 (5)	−0.0055 (5)
C2	0.0239 (6)	0.0166 (6)	0.0209 (6)	0.0085 (5)	−0.0011 (5)	0.0002 (5)
O3	0.0192 (5)	0.0203 (5)	0.0393 (6)	0.0102 (4)	−0.0003 (4)	0.0022 (4)
C3	0.0245 (6)	0.0200 (6)	0.0215 (6)	0.0128 (5)	−0.0019 (5)	0.0000 (5)
O4	0.0202 (5)	0.0162 (4)	0.0347 (5)	0.0075 (4)	−0.0003 (4)	0.0005 (4)
C4	0.0190 (6)	0.0221 (6)	0.0214 (6)	0.0101 (5)	−0.0005 (5)	0.0004 (5)
C5	0.0223 (6)	0.0186 (6)	0.0199 (6)	0.0087 (5)	−0.0014 (5)	−0.0006 (5)
C6	0.0230 (6)	0.0177 (6)	0.0220 (6)	0.0110 (5)	−0.0011 (5)	−0.0013 (5)
C7	0.0261 (7)	0.0166 (6)	0.0250 (6)	0.0092 (5)	−0.0019 (5)	−0.0018 (5)
C8	0.0229 (7)	0.0235 (7)	0.0380 (8)	0.0105 (6)	−0.0026 (6)	−0.0020 (6)
C9	0.0244 (7)	0.0240 (6)	0.0309 (7)	0.0149 (6)	−0.0005 (5)	0.0022 (5)
C10	0.0225 (7)	0.0295 (7)	0.0496 (9)	0.0136 (6)	0.0007 (6)	0.0032 (6)
C11	0.0307 (8)	0.0336 (8)	0.0846 (13)	0.0199 (7)	−0.0147 (8)	−0.0088 (8)
C12	0.0256 (7)	0.0188 (6)	0.0289 (7)	0.0123 (5)	0.0001 (5)	−0.0003 (5)
C13	0.0264 (7)	0.0204 (7)	0.0366 (7)	0.0089 (6)	−0.0018 (6)	−0.0015 (6)
C14	0.0381 (8)	0.0195 (7)	0.0520 (10)	0.0124 (6)	0.0014 (7)	0.0003 (6)

Geometric parameters (Å, º)

O1—N1	1.2262 (14)	C9—C10	1.5037 (18)
N1—O2	1.2255 (14)	C9—H9A	0.9900
N1—C2	1.4619 (16)	C9—H9B	0.9900
C1—C2	1.3955 (17)	C10—C11	1.523 (2)
C1—C6	1.4108 (16)	C10—H10A	0.9900
C1—C7	1.4361 (18)	C10—H10B	0.9900
C2—C3	1.3963 (18)	C11—H11A	0.9800
O3—C4	1.3587 (14)	C11—H11B	0.9800
O3—C9	1.4476 (15)	C11—H11C	0.9800
C3—C4	1.3831 (17)	C12—C13	1.5087 (17)
C3—H3	0.936 (14)	C12—H12A	0.9900
O4—C5	1.3527 (15)	C12—H12B	0.9900
O4—C12	1.4422 (14)	C13—C14	1.5191 (19)
C4—C5	1.4148 (17)	C13—H13A	0.9900
C5—C6	1.3796 (17)	C13—H13B	0.9900
C6—H6	0.9500	C14—H14A	0.9800
C7—C8	1.1862 (19)	C14—H14B	0.9800
C8—H8	0.935 (9)	C14—H14C	0.9800

O2—N1—O1	123.12 (11)	C9—C10—C11	111.07 (12)
O2—N1—C2	118.26 (11)	C9—C10—H10A	109.4
O1—N1—C2	118.62 (10)	C11—C10—H10A	109.4
C2—C1—C6	116.55 (11)	C9—C10—H10B	109.4
C2—C1—C7	126.96 (11)	C11—C10—H10B	109.4
C6—C1—C7	116.46 (10)	H10A—C10—H10B	108.0
C1—C2—C3	122.61 (11)	C10—C11—H11A	109.5
C1—C2—N1	120.76 (11)	C10—C11—H11B	109.5
C3—C2—N1	116.62 (11)	H11A—C11—H11B	109.5
C4—O3—C9	117.71 (9)	C10—C11—H11C	109.5
C4—C3—C2	119.58 (11)	H11A—C11—H11C	109.5
C4—C3—H3	120.8 (11)	H11B—C11—H11C	109.5
C2—C3—H3	119.5 (11)	O4—C12—C13	108.62 (10)
C5—O4—C12	116.89 (10)	O4—C12—H12A	110.0
O3—C4—C3	125.21 (11)	C13—C12—H12A	110.0
O3—C4—C5	115.38 (10)	O4—C12—H12B	110.0
C3—C4—C5	119.40 (11)	C13—C12—H12B	110.0
O4—C5—C6	124.60 (11)	H12A—C12—H12B	108.3
O4—C5—C4	115.58 (10)	C12—C13—C14	109.95 (12)
C6—C5—C4	119.82 (11)	C12—C13—H13A	109.7
C5—C6—C1	122.02 (11)	C14—C13—H13A	109.7
C5—C6—H6	119.0	C12—C13—H13B	109.7
C1—C6—H6	119.0	C14—C13—H13B	109.7
C8—C7—C1	170.34 (13)	H13A—C13—H13B	108.2
C7—C8—H8	179.0 (11)	C13—C14—H14A	109.5
O3—C9—C10	107.23 (10)	C13—C14—H14B	109.5
O3—C9—H9A	110.3	H14A—C14—H14B	109.5
C10—C9—H9A	110.3	C13—C14—H14C	109.5
O3—C9—H9B	110.3	H14A—C14—H14C	109.5
C10—C9—H9B	110.3	H14B—C14—H14C	109.5
H9A—C9—H9B	108.5		

C3—C2—N1—O2	17.89 (17)	C1—C2—N1—O1	18.77 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O3^{i}	0.94 (1)	2.48 (1)	3.4001 (16)	167 (2)
C8—H8···O4^{i}	0.94 (1)	2.62 (2)	3.3267 (16)	133 (1)
C3—H3···O2^{ii}	0.94 (1)	2.61 (1)	3.5459 (16)	177 (2)

Symmetry codes: (i) $y+1/3, -x+y+2/3, -z+2/3$; (ii) $-x+4/3, -y+5/3, -z+2/3$.

1,2-dibutoxy-4-ethynyl-5-nitrobenzene (2)

Crystal data

$C_{16}H_{21}NO_4$	a = 8.5209 (5) Å
M_r = 291.34	b = 18.0914 (10) Å
Monoclinic, $P2_1/c$	c = 9.9579 (5) Å

β = 97.967 (1)°
V = 1520.24 (14) Å^3
Z = 4
F(000) = 624
D_x = 1.273 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3448 reflections
θ = 2.3–26.4°
μ = 0.09 mm^{-1}
T = 100 K
Irregular block, colourless
0.60 × 0.34 × 0.02 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS Version 2014; Bruker AXS)
$T_{\min}$ = 0.682, $T_{\max}$ = 0.746
19579 measured reflections
3370 independent reflections
2449 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
$\theta_{\max}$ = 27.2°, $\theta_{\min}$ = 2.3°
$h = -10 \rightarrow 10$
$k = -23 \rightarrow 23$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.103
S = 1.02
3370 reflections
198 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.5063P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.25 e Å^{-3}
$\Delta\rho_{\min}$ = −0.18 e Å^{-3}

Special details

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

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

	x	y	z	U_{iso}*/U_{eq}
O1	0.24462 (15)	0.41330 (6)	−0.09599 (12)	0.0331 (3)
N1	0.22644 (15)	0.34657 (7)	−0.09358 (12)	0.0194 (3)
C1	0.41750 (17)	0.33670 (8)	0.12054 (14)	0.0153 (3)
O2	0.13376 (14)	0.31327 (7)	−0.17849 (12)	0.0335 (3)
C2	0.31940 (17)	0.30296 (8)	0.01366 (14)	0.0153 (3)
O3	0.38628 (12)	0.10631 (5)	0.09739 (10)	0.0170 (2)
C3	0.30591 (17)	0.22633 (8)	0.00230 (14)	0.0156 (3)
H3	0.2381 (18)	0.2081 (9)	−0.0705 (14)	0.019*
H8	0.4862 (18)	0.5273 (7)	0.1967 (15)	0.019*
O4	0.57880 (12)	0.16462 (5)	0.28966 (10)	0.0169 (2)
C4	0.39137 (16)	0.18124 (8)	0.09726 (14)	0.0146 (3)
C5	0.49571 (16)	0.21339 (8)	0.20434 (14)	0.0145 (3)
C6	0.50568 (17)	0.28947 (8)	0.21533 (14)	0.0150 (3)
H6	0.573938	0.310557	0.288897	0.018*
C7	0.43705 (17)	0.41478 (8)	0.14269 (14)	0.0183 (3)

C8	0.46506 (19)	0.47713 (9)	0.17401 (16)	0.0227 (3)
C9	0.27503 (17)	0.07150 (8)	−0.00558 (14)	0.0168 (3)
H9A	0.307039	0.079990	−0.096176	0.020*
H9B	0.167922	0.092592	−0.005009	0.020*
C10	0.27354 (17)	−0.01003 (8)	0.02436 (14)	0.0167 (3)
H10A	0.236740	−0.017855	0.113319	0.020*
H10B	0.382713	−0.029677	0.030183	0.020*
C11	0.16582 (18)	−0.05231 (8)	−0.08441 (15)	0.0190 (3)
H11A	0.057299	−0.031722	−0.092033	0.023*
H11B	0.204412	−0.045622	−0.172931	0.023*
C12	0.16069 (19)	−0.13435 (8)	−0.05226 (16)	0.0231 (4)
H12A	0.266801	−0.155571	−0.050285	0.035*
H12B	0.086938	−0.159234	−0.122124	0.035*
H12C	0.125019	−0.141126	0.036353	0.035*
C13	0.69850 (17)	0.19390 (8)	0.39333 (14)	0.0161 (3)
H13A	0.648403	0.224452	0.458108	0.019*
H13B	0.773813	0.225262	0.351626	0.019*
C14	0.78460 (17)	0.12937 (8)	0.46602 (14)	0.0175 (3)
H14A	0.844815	0.102735	0.402880	0.021*
H14B	0.706485	0.094605	0.495658	0.021*
C15	0.89834 (18)	0.15516 (9)	0.58933 (15)	0.0200 (3)
H15A	0.974564	0.190909	0.559722	0.024*
H15B	0.837535	0.180877	0.653162	0.024*
C16	0.9892 (2)	0.09090 (10)	0.66219 (17)	0.0288 (4)
H16A	0.914086	0.055400	0.691711	0.043*
H16B	1.059132	0.109511	0.741391	0.043*
H16C	1.052701	0.066468	0.600332	0.043*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0427 (8)	0.0206 (7)	0.0324 (7)	0.0030 (5)	−0.0069 (6)	0.0077 (5)
N1	0.0194 (7)	0.0200 (7)	0.0184 (7)	0.0039 (5)	0.0015 (5)	0.0017 (5)
C1	0.0153 (7)	0.0148 (7)	0.0164 (7)	−0.0001 (6)	0.0039 (6)	0.0014 (6)
O2	0.0371 (7)	0.0301 (7)	0.0271 (6)	0.0032 (5)	−0.0167 (5)	−0.0001 (5)
C2	0.0147 (7)	0.0178 (8)	0.0136 (7)	0.0037 (6)	0.0021 (6)	0.0032 (6)
O3	0.0199 (5)	0.0123 (5)	0.0169 (5)	−0.0012 (4)	−0.0043 (4)	−0.0008 (4)
C3	0.0132 (7)	0.0193 (8)	0.0137 (7)	−0.0004 (6)	0.0002 (6)	−0.0016 (6)
O4	0.0198 (5)	0.0130 (5)	0.0155 (5)	−0.0010 (4)	−0.0060 (4)	0.0011 (4)
C4	0.0137 (7)	0.0159 (7)	0.0145 (7)	0.0001 (6)	0.0022 (5)	−0.0002 (6)
C5	0.0139 (7)	0.0163 (7)	0.0128 (7)	0.0015 (6)	0.0006 (5)	0.0021 (6)
C6	0.0138 (7)	0.0181 (8)	0.0130 (7)	−0.0011 (6)	0.0008 (5)	−0.0010 (6)
C7	0.0179 (8)	0.0208 (8)	0.0156 (7)	0.0029 (6)	0.0006 (6)	0.0035 (6)
C8	0.0261 (9)	0.0172 (8)	0.0235 (8)	0.0015 (7)	−0.0016 (6)	0.0026 (7)
C9	0.0152 (7)	0.0184 (8)	0.0152 (7)	−0.0011 (6)	−0.0032 (6)	−0.0015 (6)
C10	0.0152 (7)	0.0165 (8)	0.0172 (7)	−0.0002 (6)	−0.0018 (6)	−0.0001 (6)
C11	0.0207 (8)	0.0163 (8)	0.0186 (7)	0.0000 (6)	−0.0022 (6)	−0.0018 (6)
C12	0.0237 (8)	0.0184 (8)	0.0257 (8)	−0.0008 (6)	−0.0026 (7)	−0.0012 (7)

C13	0.0167 (7)	0.0161 (7)	0.0143 (7)	−0.0031 (6)	−0.0025 (6)	−0.0010 (6)
C14	0.0190 (8)	0.0166 (8)	0.0156 (7)	0.0005 (6)	−0.0022 (6)	0.0006 (6)
C15	0.0183 (7)	0.0249 (9)	0.0154 (7)	0.0026 (6)	−0.0029 (6)	−0.0007 (6)
C16	0.0256 (9)	0.0363 (10)	0.0220 (8)	0.0039 (7)	−0.0056 (7)	0.0075 (7)

Geometric parameters (Å, º)

O1—N1	1.2178 (16)	C10—C11	1.5248 (19)
N1—O2	1.2314 (16)	C10—H10A	0.9900
N1—C2	1.4683 (18)	C10—H10B	0.9900
C1—C2	1.399 (2)	C11—C12	1.520 (2)
C1—C6	1.4103 (19)	C11—H11A	0.9900
C1—C7	1.436 (2)	C11—H11B	0.9900
C2—C3	1.394 (2)	C12—H12A	0.9800
O3—C4	1.3564 (17)	C12—H12B	0.9800
O3—C9	1.4412 (16)	C12—H12C	0.9800
C3—C4	1.378 (2)	C13—C14	1.509 (2)
C3—H3	0.923 (13)	C13—H13A	0.9900
O4—C5	1.3546 (16)	C13—H13B	0.9900
O4—C13	1.4473 (16)	C14—C15	1.5281 (19)
C4—C5	1.4152 (19)	C14—H14A	0.9900
C5—C6	1.382 (2)	C14—H14B	0.9900
C6—H6	0.9500	C15—C16	1.524 (2)
C7—C8	1.186 (2)	C15—H15A	0.9900
C8—H8	0.947 (13)	C15—H15B	0.9900
C9—C10	1.505 (2)	C16—H16A	0.9800
C9—H9A	0.9900	C16—H16B	0.9800
C9—H9B	0.9900	C16—H16C	0.9800
O1—N1—O2	122.87 (13)	C12—C11—C10	111.85 (12)
O1—N1—C2	119.33 (12)	C12—C11—H11A	109.2
O2—N1—C2	117.80 (12)	C10—C11—H11A	109.2
C2—C1—C6	116.84 (13)	C12—C11—H11B	109.2
C2—C1—C7	126.19 (13)	C10—C11—H11B	109.2
C6—C1—C7	116.97 (13)	H11A—C11—H11B	107.9
C3—C2—C1	121.96 (13)	C11—C12—H12A	109.5
C3—C2—N1	116.44 (13)	C11—C12—H12B	109.5
C1—C2—N1	121.60 (13)	H12A—C12—H12B	109.5
C4—O3—C9	117.00 (11)	C11—C12—H12C	109.5
C4—C3—C2	120.21 (13)	H12A—C12—H12C	109.5
C4—C3—H3	122.8 (10)	H12B—C12—H12C	109.5
C2—C3—H3	117.0 (10)	O4—C13—C14	107.86 (11)
C5—O4—C13	117.67 (11)	O4—C13—H13A	110.1
O3—C4—C3	125.34 (13)	C14—C13—H13A	110.1
O3—C4—C5	115.27 (12)	O4—C13—H13B	110.1
C3—C4—C5	119.39 (13)	C14—C13—H13B	110.1
O4—C5—C6	125.30 (13)	H13A—C13—H13B	108.4
O4—C5—C4	115.09 (12)	C13—C14—C15	111.17 (12)

C6—C5—C4	119.61 (13)	C13—C14—H14A	109.4
C5—C6—C1	121.94 (13)	C15—C14—H14A	109.4
C5—C6—H6	119.0	C13—C14—H14B	109.4
C1—C6—H6	119.0	C15—C14—H14B	109.4
C8—C7—C1	172.37 (16)	H14A—C14—H14B	108.0
C7—C8—H8	178.5 (10)	C16—C15—C14	111.92 (13)
O3—C9—C10	108.06 (11)	C16—C15—H15A	109.2
O3—C9—H9A	110.1	C14—C15—H15A	109.2
C10—C9—H9A	110.1	C16—C15—H15B	109.2
O3—C9—H9B	110.1	C14—C15—H15B	109.2
C10—C9—H9B	110.1	H15A—C15—H15B	107.9
H9A—C9—H9B	108.4	C15—C16—H16A	109.5
C9—C10—C11	111.82 (12)	C15—C16—H16B	109.5
C9—C10—H10A	109.3	H16A—C16—H16B	109.5
C11—C10—H10A	109.3	C15—C16—H16C	109.5
C9—C10—H10B	109.3	H16A—C16—H16C	109.5
C11—C10—H10B	109.3	H16B—C16—H16C	109.5
H10A—C10—H10B	107.9		

C1—C2—N1—O1	6.1 (2)	C3—C2—N1—O2	6.1 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O3^{i}	0.95 (1)	2.61 (1)	3.3835 (19)	139 (1)
C8—H8···O4^{i}	0.95 (1)	2.55 (1)	3.4371 (19)	156 (1)

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

(3)

Crystal data

$C_{18}H_{25}NO_4$
$M_r = 319.39$
Triclinic, $P\overline{1}$
$a = 4.570\ (4)$ Å
$b = 9.415\ (8)$ Å
$c = 20.968\ (18)$ Å
$\alpha = 94.003\ (12)°$
$\beta = 90.758\ (12)°$
$\gamma = 93.435\ (11)°$
$V = 898.2\ (14)$ Å^3

$Z = 2$
$F(000) = 344$
$D_x = 1.181$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 852 reflections
$\theta = 2.3–25.6°$
$\mu = 0.08$ mm^{-1}
$T = 100$ K
Square, colourless
0.46 × 0.14 × 0.14 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3660 pixels mm^{-1}
φ and ω scans

Absorption correction: multi-scan (SADABS Version 2014; Bruker AXS)
$T_{min} = 0.382$, $T_{max} = 0.746$
5380 measured reflections
2914 independent reflections
1604 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$

$\theta_{\max} = 24.4°$, $\theta_{\min} = 2.0°$
$h = -5 \rightarrow 5$
$k = -10 \rightarrow 10$
$l = -24 \rightarrow 23$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.085$
$wR(F^2) = 0.262$
$S = 1.03$
2914 reflections
216 parameters
2 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1254P)^2 + 0.8636P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.32$ e Å^{-3}

Special details

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

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.5970 (9)	0.2146 (5)	0.48201 (18)	0.0588 (11)
N1	0.4403 (9)	0.2986 (5)	0.5092 (2)	0.0370 (10)
C1	0.6541 (10)	0.2513 (5)	0.6159 (2)	0.0315 (12)
O2	0.2526 (9)	0.3609 (5)	0.48100 (18)	0.0590 (12)
C2	0.4709 (10)	0.3307 (5)	0.5786 (2)	0.0295 (11)
O3	0.1873 (6)	0.5814 (3)	0.70199 (15)	0.0326 (8)
C3	0.3139 (10)	0.4410 (5)	0.6053 (2)	0.0298 (11)
O4	0.5189 (7)	0.4440 (3)	0.77303 (15)	0.0345 (9)
C4	0.3319 (9)	0.4762 (5)	0.6707 (2)	0.0266 (11)
C5	0.5148 (9)	0.4001 (5)	0.7095 (2)	0.0290 (11)
C6	0.6704 (10)	0.2917 (5)	0.6818 (2)	0.0310 (11)
H6	0.793656	0.242129	0.708311	0.037*
C7	0.8201 (11)	0.1340 (5)	0.5926 (2)	0.0363 (12)
C8	0.9653 (13)	0.0361 (6)	0.5791 (3)	0.0473 (14)
C9	0.0258 (10)	0.6727 (5)	0.6633 (2)	0.0330 (12)
H9A	−0.122640	0.615029	0.636202	0.040*
H9B	0.160789	0.724363	0.635096	0.040*
C10	−0.1205 (10)	0.7763 (5)	0.7078 (2)	0.0345 (12)
H10A	−0.249033	0.721845	0.736309	0.041*
H10B	−0.247428	0.833281	0.682280	0.041*
C11	0.0872 (10)	0.8788 (5)	0.7493 (2)	0.0379 (13)
H11A	0.224340	0.822607	0.772683	0.045*
H11B	0.204592	0.939463	0.721230	0.045*
C12	−0.0696 (10)	0.9732 (5)	0.7969 (3)	0.0406 (13)
H12A	−0.184891	0.912351	0.825290	0.049*
H12B	−0.208957	1.028117	0.773504	0.049*
C13	0.1374 (13)	1.0785 (6)	0.8384 (3)	0.0603 (17)
H13A	0.275222	1.025110	0.862082	0.090*

H13B	0.021880	1.135181	0.868596	0.090*
H13C	0.246599	1.141996	0.810842	0.090*
C14	0.7373 (11)	0.3898 (5)	0.8135 (2)	0.0354 (12)
H14A	0.936232	0.418935	0.799172	0.043*
H14B	0.716549	0.284282	0.811463	0.043*
C15	0.6920 (12)	0.4506 (5)	0.8810 (2)	0.0420 (13)
H15A	0.828665	0.407640	0.910064	0.050*
H15B	0.489858	0.422903	0.893716	0.050*
C16	0.7393 (14)	0.6118 (6)	0.8896 (3)	0.0523 (16)
H16A	0.606104	0.655330	0.859921	0.063*
H16B	0.943233	0.639925	0.878241	0.063*
C17	0.6833 (16)	0.6703 (6)	0.9585 (3)	0.0654 (18)
H17A	0.479985	0.640869	0.969787	0.078*
H17B	0.817275	0.626639	0.987940	0.078*
C18	0.726 (2)	0.8298 (8)	0.9686 (3)	0.111 (3)
H18A	0.928128	0.859964	0.958565	0.167*
H18B	0.687568	0.859377	1.013337	0.167*
H18C	0.590164	0.874182	0.940628	0.167*
H3	0.187 (15)	0.483 (8)	0.578 (3)	0.133*
H8	1.065 (17)	−0.045 (6)	0.564 (4)	0.133*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.069 (3)	0.063 (3)	0.044 (2)	0.018 (2)	0.000 (2)	−0.006 (2)
N1	0.035 (2)	0.031 (2)	0.043 (3)	−0.010 (2)	−0.003 (2)	0.003 (2)
C1	0.028 (3)	0.029 (3)	0.036 (3)	−0.012 (2)	0.003 (2)	0.002 (2)
O2	0.068 (3)	0.067 (3)	0.041 (2)	0.005 (2)	−0.013 (2)	0.002 (2)
C2	0.028 (3)	0.026 (3)	0.033 (3)	−0.013 (2)	−0.002 (2)	0.003 (2)
O3	0.0285 (18)	0.0289 (18)	0.040 (2)	−0.0013 (14)	−0.0064 (14)	0.0051 (15)
C3	0.024 (2)	0.026 (3)	0.038 (3)	−0.011 (2)	−0.004 (2)	0.006 (2)
O4	0.0329 (18)	0.037 (2)	0.0327 (19)	−0.0043 (15)	−0.0057 (14)	0.0033 (15)
C4	0.022 (2)	0.020 (2)	0.037 (3)	−0.0078 (19)	0.002 (2)	0.005 (2)
C5	0.023 (2)	0.027 (3)	0.036 (3)	−0.011 (2)	−0.002 (2)	0.005 (2)
C6	0.025 (3)	0.027 (3)	0.040 (3)	−0.007 (2)	−0.004 (2)	0.006 (2)
C7	0.037 (3)	0.029 (3)	0.041 (3)	−0.010 (2)	0.001 (2)	0.001 (2)
C8	0.061 (4)	0.039 (3)	0.041 (3)	−0.003 (3)	0.002 (3)	0.001 (3)
C9	0.023 (2)	0.032 (3)	0.044 (3)	0.003 (2)	−0.003 (2)	0.007 (2)
C10	0.025 (3)	0.029 (3)	0.050 (3)	−0.003 (2)	−0.002 (2)	0.012 (2)
C11	0.030 (3)	0.030 (3)	0.054 (3)	−0.002 (2)	0.000 (2)	0.007 (2)
C12	0.032 (3)	0.030 (3)	0.060 (3)	−0.001 (2)	−0.002 (2)	0.009 (2)
C13	0.053 (4)	0.045 (4)	0.080 (4)	0.001 (3)	−0.010 (3)	−0.010 (3)
C14	0.037 (3)	0.032 (3)	0.037 (3)	−0.005 (2)	−0.007 (2)	0.008 (2)
C15	0.048 (3)	0.042 (3)	0.035 (3)	−0.009 (2)	−0.005 (2)	0.007 (2)
C16	0.069 (4)	0.042 (3)	0.044 (3)	−0.014 (3)	−0.007 (3)	0.001 (3)
C17	0.096 (5)	0.052 (4)	0.047 (4)	0.002 (4)	−0.008 (3)	−0.005 (3)
C18	0.210 (11)	0.063 (5)	0.057 (5)	0.001 (6)	−0.002 (5)	−0.013 (4)

Geometric parameters (Å, º)

O1—N1	1.215 (5)	C11—C12	1.507 (7)
N1—O2	1.234 (5)	C11—H11A	0.9900
N1—C2	1.469 (6)	C11—H11B	0.9900
C1—C6	1.408 (6)	C12—C13	1.542 (7)
C1—C2	1.418 (7)	C12—H12A	0.9900
C1—C7	1.438 (7)	C12—H12B	0.9900
C2—C3	1.388 (7)	C13—H13A	0.9800
O3—C4	1.359 (5)	C13—H13B	0.9800
O3—C9	1.449 (5)	C13—H13C	0.9800
C3—C4	1.388 (7)	C14—C15	1.511 (7)
C3—H3	0.93 (2)	C14—H14A	0.9900
O4—C5	1.366 (5)	C14—H14B	0.9900
O4—C14	1.440 (6)	C15—C16	1.518 (7)
C4—C5	1.417 (6)	C15—H15A	0.9900
C5—C6	1.379 (6)	C15—H15B	0.9900
C6—H6	0.9500	C16—C17	1.540 (8)
C7—C8	1.188 (7)	C16—H16A	0.9900
C8—H8	0.95 (2)	C16—H16B	0.9900
C9—C10	1.496 (6)	C17—C18	1.503 (9)
C9—H9A	0.9900	C17—H17A	0.9900
C9—H9B	0.9900	C17—H17B	0.9900
C10—C11	1.529 (6)	C18—H18A	0.9800
C10—H10A	0.9900	C18—H18B	0.9800
C10—H10B	0.9900	C18—H18C	0.9800

O1—N1—O2	123.0 (4)	C11—C12—C13	113.8 (4)
O1—N1—C2	120.1 (4)	C11—C12—H12A	108.8
O2—N1—C2	116.9 (4)	C13—C12—H12A	108.8
C6—C1—C2	116.1 (4)	C11—C12—H12B	108.8
C6—C1—C7	117.8 (5)	C13—C12—H12B	108.8
C2—C1—C7	126.1 (4)	H12A—C12—H12B	107.7
C3—C2—C1	122.2 (4)	C12—C13—H13A	109.5
C3—C2—N1	117.1 (4)	C12—C13—H13B	109.5
C1—C2—N1	120.7 (4)	H13A—C13—H13B	109.5
C4—O3—C9	117.2 (4)	C12—C13—H13C	109.5
C2—C3—C4	120.0 (4)	H13A—C13—H13C	109.5
C2—C3—H3	117 (5)	H13B—C13—H13C	109.5
C4—C3—H3	123 (5)	O4—C14—C15	107.7 (4)
C5—O4—C14	117.8 (4)	O4—C14—H14A	110.2
O3—C4—C3	125.0 (4)	C15—C14—H14A	110.2
O3—C4—C5	115.5 (4)	O4—C14—H14B	110.2
C3—C4—C5	119.4 (4)	C15—C14—H14B	110.2
O4—C5—C6	125.7 (4)	H14A—C14—H14B	108.5
O4—C5—C4	114.8 (4)	C14—C15—C16	113.9 (4)
C6—C5—C4	119.5 (4)	C14—C15—H15A	108.8
C5—C6—C1	122.7 (5)	C16—C15—H15A	108.8

C5—C6—H6	118.7	C14—C15—H15B	108.8
C1—C6—H6	118.7	C16—C15—H15B	108.8
C8—C7—C1	173.9 (6)	H15A—C15—H15B	107.7
C7—C8—H8	173 (5)	C15—C16—C17	112.4 (5)
O3—C9—C10	107.5 (4)	C15—C16—H16A	109.1
O3—C9—H9A	110.2	C17—C16—H16A	109.1
C10—C9—H9A	110.2	C15—C16—H16B	109.1
O3—C9—H9B	110.2	C17—C16—H16B	109.1
C10—C9—H9B	110.2	H16A—C16—H16B	107.8
H9A—C9—H9B	108.5	C18—C17—C16	113.9 (6)
C9—C10—C11	115.2 (4)	C18—C17—H17A	108.8
C9—C10—H10A	108.5	C16—C17—H17A	108.8
C11—C10—H10A	108.5	C18—C17—H17B	108.8
C9—C10—H10B	108.5	C16—C17—H17B	108.8
C11—C10—H10B	108.5	H17A—C17—H17B	107.7
H10A—C10—H10B	107.5	C17—C18—H18A	109.5
C12—C11—C10	113.3 (4)	C17—C18—H18B	109.5
C12—C11—H11A	108.9	H18A—C18—H18B	109.5
C10—C11—H11A	108.9	C17—C18—H18C	109.5
C12—C11—H11B	108.9	H18A—C18—H18C	109.5
C10—C11—H11B	108.9	H18B—C18—H18C	109.5
H11A—C11—H11B	107.7		

C1—C2—N1—O1	−8.4 (6)	C3—C2—N1—O2	−8.0 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O2^{i}	0.93 (2)	2.88 (3)	3.793 (7)	167 (7)
C9—H9*A*···O2^{i}	0.99	2.55	3.254 (7)	128
C8—H8···O1^{ii}	0.95 (2)	2.45 (3)	3.381 (8)	167 (8)

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