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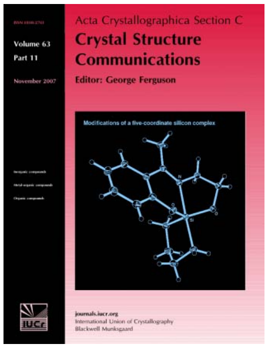

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Interaction between an oxygen and an alkynyl-carbon atom in 1-(2-nitrophenyl)-4-phenylbutadiyne

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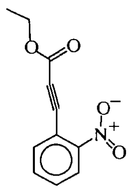
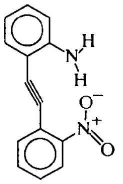
Abstract

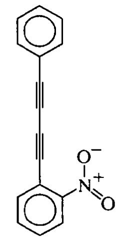
The title compound, $C_{16}H_9NO_2$, studied at 122 K shows a short 1,5 interaction between a nitro-O atom and an alkynyl-C atom. The atomic separation is 2.636 (2) Å, and the dialkyne group is bent from linearity at this C atom only.

Comment

The study of the molecular distortions induced by placing a nucleophilic functional group close to an electrophilic functional group in the same molecule has given insight into the early stages of reaction coordinates (Bürgi & Dunitz, 1994). For example, in *peri*-substituted naphthalenes bearing a dimethylamino group and a carbonyl-containing functional group, the 1,5 interaction between the amino-N atom and carbonyl-C atom models an early stage in the addition of a nucleophile to the carbonyl bond and small pyramidalizations of the carbonyl-C atom's bonding geometry are observed (Schweizer *et al.*, 1978). We have been investigating interactions involving alkyne groups (Pilkington *et al.*, 1995). 1,5 interactions between nitro-O atoms and alkynyl-C atoms have been observed in (I) and (II), both of which show *trans* distortions of the triple bonds, as shown in the structural formulae (Rice & Wallis, 1993; Pilkington *et al.*, 1996). Analysis of the results of *ab initio* calculations on (II) using Bader's theory of atoms in molecules (Bader, 1990) gives evidence of a weak bonding interaction between the nitro-O and alkynyl-C atoms (Pilkington *et al.*, 1996). These interactions may be interpreted as representing the structural consequences of an incipient Michael addition reaction. The structure of the title compound (III), which contains a dialkyne rather than an alkyne group, was determined to extend this investigation.


(I)


(II)


(III)

The overall structure is almost planar, and the interplanar angle between the nitro group and the attached aromatic ring is only 9.93 (16)°. As in (I) and (II) there is a short 1,5 contact between a nitro-O atom and the closest C atom of the dialkyne group. The distance between these atoms is 2.636 (2) Å, and is very similar to those in (I) [2.642 (2) Å] and (II) [2.662 (4) and 2.772 (4) Å]. The dialkyne group deviates from linearity by 7.28 (13)° at the C atom involved in the interaction such that this C atom is displaced from the vector connecting its two neighbours towards the O atom. However, unlike the structures of (I) and (II), there is no significant deviation from linearity at any of the other three C*sp* atoms, where the bond angles lie in the range 178.60 (13) to 179.43 (13)°. There is no difference in the bond lengths of the two alkyne groups [1.203 (2) Å]. Furthermore, the structure contains no unusually short intermolecular contacts.

In structures (I) and (II), the bending induced at the alkyne-C atom not directly involved in the interaction is interpreted as being due to the start of the development of in-plane sp^2 lone-pair electron density as a result of the incipient nucleophilic addition to the other end of the triple bond. In (III), this feature need not be so localized since the developing lone-pair electron density would be able to conjugate with the π system of the second triple bond. This would account for the absence of a second bend in the dialkyne group. Alternatively, it could be argued that only a single bend is required to minimize repulsion between the two groups and, in particular, to increase the distance between O1 and the second alkyne-C atom, C2, to 3.201 (2) Å. However, if repulsive interactions were operating at *ca* 3.0 Å, it would have been expected that the nitro group would have rotated

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out of coplanarity with the molecule to relieve the much shorter, and presumably more repulsive, O1· · ·C1 contact. In fact, the *ortho* substituents are splayed apart in the plane of the molecule, but this only indicates that the O1· · ·C1 interaction is repulsive at separations below 2.636 (2) Å.

Four known dialkyne structures which contain intramolecular 1,5 O· · ·C*sp* contacts show longer O· · ·C distances (2.81–2.98 Å) than in (III), and no pronounced bending at the involved C*sp* atom (Hanson, 1975; Lu *et al.*, 1993; Bott *et al.*, 1995; Kane *et al.*, 1995). In each case the O atom involved belongs to a carbonyl group.

A search of the Cambridge Structural Database (Allen *et al.*, 1991) revealed that dialkyne groups in acyclic molecular fragments are usually close to linear; of 117 hits ($R < 10\%$, no errors or disorder) 68% show angular deviations at the alkyne-C atoms of no more than 4°. Some of the larger angular distortions (of up to 10° at the termini of the dialkyne moiety) are observed in Toda's clathrates of 1,6-bis(2-chlorophenyl)-1,6-diphenylbuta-2,4-diyn-1,6-diol. They are associated with 1,5 Cl· · ·C*sp* contacts of *ca* 3.1 Å [*e.g.* GIMKIW (Kaftory *et al.*, 1988) and VAXFUV (Toda *et al.*, 1989)]. When restrained in a cyclic structure, a dialkyne group can be bent by up to 15° from linearity at any one C atom [*e.g.* FECDAS (Kaftory *et al.*, 1987) and PECBAA (Anthony *et al.*, 1993)].

It is important to recognize that a final conclusion about the type of nitro/dialkyne interaction observed in (III) can only be made from a series of structures, since the crystal packing arrangement could be responsible for small distortions to a particular molecular structure.

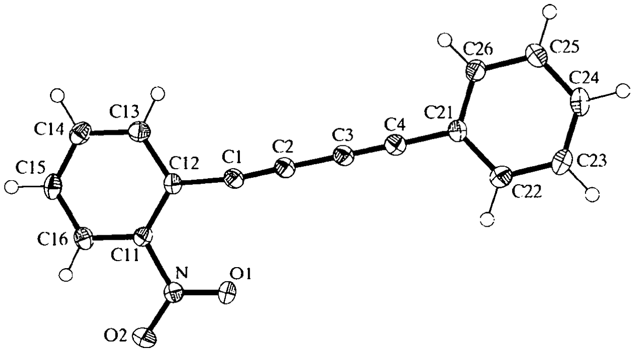

Fig. 1. *ORTEP*III (Johnson & Burnett, 1996) drawing of the title compound. Anisotropic displacement parameters are drawn at the 50% level for non-H atoms and circles of an arbitrary radius depict H atoms.

Experimental

Substance (III) was prepared by the coupling of ethynylbenzene with 1-bromoethynyl-2-nitrobenzene using a copper(I) chloride catalyst and hydroxylamine hydrochloride in ethanolic ethylamine, as described for other cases (Tsibouklis *et al.*, 1988); m.p. 433 K, ^{1}H NMR (270 MHz, $CDCl_3$): 8.13 (1H, *dd*, *J* 8.1, 1.3, 3′-H), 7.74 (1H, *dd*, *J* 7.7, 1.6, 6′-H), 7.61 (1H, *dt*, *J* 7.5, 1.3, 5′-H), 7.56 (2H, *dd*, *J* 7.9, 1.7, 2″-, 6″-H), 7.51 (1H, *dt*, *J* 7.7, 1.5, 4′-H), 7.38 p.p.m. (3H, *m*, 3″-, 4″-, 5″-H), ^{13}C NMR (67.8 MHz $CDCl_3$): 150.1 (2′-C), 135.9 (5′-C), 133.0 (6′-C), 132.7 (2″-, 6″-C), 129.7 (4′-C), 129.3 (4″-C), 128.5 (3″-, 5″-C), 125.0 (3′-C), 121.3 (1″-C), 117.8 (1′-C), 84.9, 81.6, 76.1, 73.7 p.p.m. (1-, 2-, 3-, 4-C).

Crystal data

$C_{16}H_9NO_2$
$M_r = 247.24$
Orthorhombic
Pbca
$a = 7.532\,(5)$ Å
$b = 13.278\,(2)$ Å
$c = 23.7103\,(10)$ Å
$V = 2371.3\,(16)$ Å^3
$Z = 8$
$D_x = 1.385$ Mg m^{-3} (at 122 K)
$D_m = 1.305$ Mg m^{-3} (measured at 295 K)
D_m measured by flotation in aqueous KI

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 20 reflections
$\theta = 35.47–43.19°$
$\mu = 0.751$ mm^{-1}
$T = 122.0\,(5)$ K
Block
$0.38 \times 0.38 \times 0.17$ mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
6580 measured reflections
2404 independent reflections
2249 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.019$
$\theta_{\rm max} = 74.89°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 28$
5 standard reflections frequency: 166.7 min intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.089$
$S = 3.456$
2404 reflections
209 parameters
H atoms were refined freely with individual isotropic displacement parameters
$w = 1/[\sigma^2(F_o^2)]$

$(\Delta/\sigma)_{\rm max} = 0.017$
$\Delta\rho_{\rm max} = 0.246$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.236$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0041 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—N	1.2207 (14)	C4—C21	1.430 (2)
O2—N	1.2352 (14)	C11—C16	1.388 (2)
N—C11	1.467 (2)	C11—C12	1.399 (2)
C1—C2	1.203 (2)	C12—C13	1.409 (2)
C1—C12	1.428 (2)	C13—C14	1.381 (2)
C2—C3	1.371 (2)	C14—C15	1.388 (2)
C3—C4	1.203 (2)	C15—C16	1.383 (2)
O1—N—O2	122.93 (11)	C12—C11—N	120.54 (11)
O1—N—C11	118.98 (10)	C11—C12—C13	116.57 (11)
O2—N—C11	118.09 (11)	C11—C12—C1	125.38 (12)
C2—C1—C12	172.72 (13)	C13—C12—C1	118.03 (11)
C1—C2—C3	179.27 (14)	C14—C13—C12	121.35 (12)
C4—C3—C2	179.43 (13)	C13—C14—C15	120.45 (12)
C3—C4—C21	178.60 (13)	C16—C15—C14	119.79 (12)
C16—C11—C12	122.39 (12)	C15—C16—C11	119.43 (12)
C16—C11—N	117.06 (11)		

The structure was solved using direct methods and refined by the full-matrix least-squares technique. All non-H atoms were refined with anisotropic displacement parameters. Weights calculated from counting statistics were employed as it was found that they provided a reliable estimate of the experimental error. The resulting averaged values of $w(\Delta F)^2$ as a function of $\sin\theta$ and F^2 did not show any significant variations.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*III (Johnson & Burnett, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1068). Services for accessing these data are described at the back of the journal.

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1,3,5-Tris(cyanomethyl)-2,4,6-triethylbenzene

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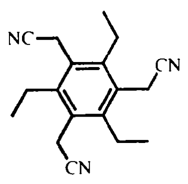
Abstract

The title compound (2,4,6-triethyl-1,3,5-benzenetriacetonitrile, $C_{18}H_{21}N_3$) exhibits an unexpected conformation with all the substituents, except one cyanomethyl group, pointing to the same side of the plane of the benzene ring.

Comment

Hexa-substituted derivatives of benzene with the substituents connected *via* methylene groups to the central benzene ring have attracted considerable interest. In general, the most stable conformation of such compounds is the one with the substituents pointing alternately to both sides (above and below) of the plane of the central benzene ring. This conformational preference has been employed in an approach to 'hexa-host' clathrate compounds (MacNicol & Downing, 1996). More recently, derivatives with ethyl groups in the 1, 3 and 5 positions and substituents that carry functional groups attached to the remaining positions of the benzene ring have been used as predisposed (Stack *et al.*, 1993; Walsdorff *et al.*, 1996; Metzger *et al.*, 1997) or preorganized (Walsdorff *et al.*, 1997) tripodal ligands, in a self-directed macrocyclization (Bisson *et al.*, 1997) and in the spontaneous self-assembly of a cage compound (Hartshorn & Steel, 1997). In the course of our ongoing research on such molecules we have determined the crystal structure of the title compound, (I).



(I)

In spite of its symmetrical constitution, (I) crystallizes on a general position in the triclinic space group

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