ORIGINAL PAPER



# X-ray Structures of 1-Ethynyl-2-Nitrobenzene and 1-Ethynyl-4,5-Dimethyl-2-Nitrobenzene: Correlation to the Enhanced Rate of Hydration and Investigation of the C–H…O Alkyne-Nitro Hydrogen Bonding

Eric Bosch<sup>1</sup><sup>(D)</sup> · Laura Jeffries<sup>1</sup>

Received: 4 June 2016/Accepted: 29 June 2016/Published online: 5 July 2016 © Springer Science+Business Media New York 2016

Abstract The single crystal X-ray structures of 2-nitrophenylacetylene, 1, and 4,5-dimethyl-2-nitrophenylacetylene, 2, are presented. In both structures the nitro moiety is essentially coplanar with the benzene ring and interacts with the proximal alkyne which is slightly distorted. The crystal packing of both compounds is dominated by intramolecular alkyne-nitro C-H--O hydrogen bonds that are supplemented by weak arene  $C-H\cdots O$  (nitro) hydrogen bonds. Compound 1 crystallizes in the monogroup P21/c clinic space with a = 3.7874(5),  $b = 13.0673(16), c = 13.98174(17) \text{ Å}, \beta = 90.587(2)$  and Z = 4. The molecule is disordered over two sites with occupancy ratio of 88:12. Compound 2 crystallizes in the triclinic space group P-1 with a = 7.6080(5), b = 9.8811(6), c = 12.8240(8) Å,  $\alpha = 108.1760(10),$  $\beta = 102.4170$ ,  $\gamma = 96.6480(10)$  and Z = 4. The intermolecular interactions in both structures were dominated by alkyne-nitro and arene-nitro C-H···O hydrogen bonds.

**Electronic supplementary material** The online version of this article (doi:10.1007/s10870-016-0660-0) contains supplementary material, which is available to authorized users.

 Eric Bosch ericbosch@missouristate.edu; http://chemistry.missouristate.edu/EricBosch.aspx **Graphical Abstract** The structures of 2-nitrophenylacetylene and 4,5-dimethyl-2-nitrophenylacetylene display a strong nitro-alkyne intramolecular O…C interaction resulting in distortion of the alkyne and terminal alkynenitro CH…O intermolecular interactions.



**Keywords** 1-ethynyl-2-nitrobenzenes  $\cdot$  C–H $\cdots$ O hydrogen bonds  $\cdot$  Alkyne-nitro supramolecular synthons

## Introduction

Some time ago we attempted the reduction of nitrophenylacetylenes using conventional reducing reagents [1]. We, unexpectedly, found that reduction of ortho-nitrophenylacetylenes did not yield the expected amino-alkyne reduction product, but rather ortho-aminoacetophenones. This one-pot reduction-hydration of o-nitrophenylacetylenes is shown in Scheme 1. In contrast the *m*-nitrophenylacetylenes are smoothly reduced to the corresponding *m*aminopehnylacetylenes suggesting an activating role for the proximal nitro moiety [2].

<sup>&</sup>lt;sup>1</sup> Chemistry Department, Missouri State University, 901 South National Avenue, Springfield, MO 65897, USA

R

 $NH_2$ 

Scheme 1 Concomitant reduction and hydration of *o*-nitrophenylacetylenes



We investigated the crystal structures of compounds 1 and 2 to gain insight into the role of the ortho-nitro substituent in enhancing the reactivity of the alkyne and also examine intermolecular interactions in geometrically demanding nitro alkynes. In this regard it is important to note that Wallace and Howard et al. [3] reported an indepth study of o-nitrophenylalkynes, including X-ray structural and gas phase computational results, describing the nucleophilic approach of the nitro-O atom to the proximal alkyne. We believed that this nucleophilic approach of the nitro group to the alkyne renders it more susceptible to hydration. We now describe the single crystal structures of o-nitrophenylacetylenes 1 and 2 that confirms the distortion of the alkynyl group by the proximal nitro group. We also describe the weak intermolecular interactions C-H...O hydrogen bonds that stabilize the three-dimensional structure.

## **Experimental**

#### Synthesis

The nitroalkynes, 1-ethynyl-2-nitrobenzene, **1**, and 1-ethynyl-4,5-dimethyl-2-nitrobenzene, **2**, were prepared as described previously [1]. Samples of **1** and **2** suitable for X-ray analysis were obtained by slow crystallization from dichloromethane.

### **X-ray Structure Determinations**

Crystals were mounted on small cryoloops using viscous hydrocarbon oil. Data were collected using a Bruker Apex2 CCD diffractometer equipped with Mo K $\alpha$  radiation with  $\lambda = 0.71073$  Å. Low temperature data collection was facilitated by use of a Kryoflex system with an accuracy of  $\pm 1$  K. Initial data processing was carried out using the Bruker SMART and SAINT software suite [4]. Structures were solved by direct methods using SHELXS-2014/7 and refined using standard alternating least-squares cycles against F2 using SHELXL-2014/7 [5]. The program X-Seed was used as a graphical interface [6]. Hydrogen

3. R = H; 4.  $R = CH_3$ atoms were found in the difference maps and were placed in idealized positions and refined with a riding model. For the solution of structure 1 the ethynyl and nitro groups were disordered over two (exchanged) positions and the disorder was modeled using a free variable which converged to 0.89. The minor component nitro and alkyne atoms were refined isotropically and one of the N–O bonds of the minor component was constrained. The asymmetric

unit of 2 contained two unique molecules. The crystallo-

graphic data for these structures is collected in Table 1.

## **Results and Discussion**

SnCl<sub>2</sub>/EtOH-H<sub>2</sub>O

#### X-ray Crystal Structures

The structure of 1-ethynyl-2-nitrobenzene, **1**, has a single unique 1-ethynyl-2-nitrobenzene molecule in the asymmetric unit as shown in Fig. 1a. The molecule is disordered over two positions with relative ratio of 89:11. The benzene of the two components overlap however the positions of the nitro and ethynyl moieties are exchanged in the two components. The structure of 1-ethynyl-4,5-dimethyl-2nitrobenzene, **2**, contains two unique 1-ethynyl-4,5-dimethyl-2-nitrobenzene molecules in the asymmetric unit as shown in Fig. 1b.

We will first focus on the orientation of the nitro group with respect to the benzene ring and the neighboring alkyne, the degree of distortion from linearity of the alkyne, and the distance between the nitro oxygen atom and the alkyne carbon using the parameters defined in Scheme 2.

The nitro group is almost coplanar with the benzene ring in compound **1** with a torsional angle of about  $0.4^{\circ}$  with a close oxygen–carbon interaction (*d1* in Scheme 1) of 2.684(6) Å. This O–C distance is significantly less than the sum of the van der Waals radii of 3.22 Å [7]. This strong interaction is also manifest in the bending of the alkyne; thus while angle  $\gamma$  is 119.9(4)° angle  $\beta$  is 126.1(5)° and angle  $\alpha$  is 173.4(9)°. In compound **2** the nitro group is also essentially coplanar with the benzene ring in both unique molecules with torsional angles of 0.2 and 0.3° with close

#### Table 1 Crystal data and structure refinement for compound 1 and 2

Compound	1	2
Empirical formula	C <sub>8</sub> H <sub>5</sub> NO <sub>2</sub>	C <sub>10</sub> H <sub>9</sub> NO <sub>2</sub>
Formula weight	147.13	175.18
Color, habit	Orange, block	Yellow, block
Temperature, K	173 (2)	173 (2)
Wavelength, source	0.71073 Å, Mo K-α	0.71073 Å, Mo K-α
Crystal system, space group	Monoclinic, P21/c	Triclinic, P-1
Unit cell dimensions		
a, (Å)	3.7874 (5)	7.6080 (5)
b, (Å)	13.0673 (16)	9.8811 (6)
c, (Å)	13.8174 (17)	12.8240 (8)
α, °	90	108.1760 (10)
β, °	90.587 (2)	102.4170 (10)
γ, <sup>ο</sup>	90	96.6480 (10)
Volume, Å <sup>3</sup>	683.80 (15)	876.98 (10)
Z, calculated density, mg/m <sup>3</sup>	4, 1.429	4, 1.327
Absorption coefficient, mm <sup>-1</sup>	0.105	0.094
F(000)	304	368
Crystal size, mm	$0.57 \times 0.21 \times 0.15$	$0.41 \times 0.25 \times 0.16$
Theta range for data collection, $^{\circ}$	2.14–27.097	1.73–27.18
Limiting indices	$-4 \le h \le 4, -16 \le k \le 16, -17 \le l \le 17$	$-9 \le h \le 9, -12 \le k \le 12, -16 \le l \le 16$
Reflections collected/unique	12,490/1503 [R(int) = 0.031]	16,790/3885 [R(int) = 0.036]
Data completeness	0.999	0.995
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.96 and 0.98	0.97 and 0.99
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1503/20/136	3885/0/239
Goodness-of-fit on F <sup>2</sup>	1.147	1.049
Final R indices $[I > 2\theta(I)]$	R1 = 0.0940, wR2 = 0.2355	R1 = 0.0467, wR2 = 0.1111
R indices (all data)	R1 = 0.1025, wR2 = 0.2391	R1 = 0.0764, wR2 = 0.1279

Fig. 1 a View of asymmetric unit in the X-ray crystal structure of the 1-ethynyl-2nitrobenzene, 1. The minor component of the disorder is not shown. b View of unique molecules in the asymmetric unit of the structure of 1-ethynyl-4,5-dimethyl-2nitrobenzene, 2. Thermal ellipsoids drawn at the 50 % level



oxygen–carbon contacts, d1, of 2.667(2) and 2.676(2) Å. Angles  $\gamma$  are 121.30(14) and 121.17(14)°, angles  $\beta$  are 125.47(15) and 125.61(15)° and angles  $\alpha$  are 175.0(2) and 175.05(18)°. These angles and distances confirm a strong interaction between the nitro group and the alkyne. A search of the Cambridge Structural Database [8] revealed 13 structures that contained the *o*-nitroethynylbenzene motif. Twelve of these 13 structures [9] have the nitro



Scheme 2 a Parameters defining the intramolecular nitro-alkyne interaction. b Space filling model of the asymmetric unit of 2-nitrophenylacetylene, 1

group essentially coplanar with the benzene ring and the alkyne-nitro C–O distances (*dl* Scheme 2a) range from 2.636 to 2.708 Å and most values for angle  $\alpha$  between 171.5 and 173.3°. The structure that does not have a

coplanar nitro group (CCDC Ref code RUXZIU) does not exhibit significant deformation of the alkyne [10].

While it is reasonable that the nitro moiety departs from the near planar arrangement in solution it is nonetheless likely that this strong intramolecular interaction between the nucleophilic oxygen atom and the alkyne renders the terminal carbon more susceptible to protonation (or interaction with a Lewis acid) and subsequent facile hydration in solution as shown in Scheme 3. This would explain the ease with which ortho-nitroalkynes are hydrated during reduction of the nitro group in contrast to selective reduction of the nitro group in the meta-nitro analogues.

The crystal packing of *o*-nitro phenylacetylenes **1** and **2** revealed weak alkyne-nitro C–H···O interactions. For example in the packing of 2-nitrophenylacetylene, **1**, a two-dimensional corrugated sheet was formed with two nitro C–H···O interactions. The stronger of these interactions is an asymmetric alkyne C–H···O (nitro) interaction that links molecules of **1** in a zig-zag arrangement as shown in Fig. 2 as "**a**". The H8···O2 distance is 2.434(6) Å and the C–



Scheme 3 Proposed partial pathway for nitro-assisted hydration of phenyl acetylene concomitant with reduction of the nitro group



Fig. 2 Crystal packing of compound 1 showing the corrugated two-dimensional sheets formed with the dominant asymmetric alkyne C-H…nitro interaction (a) and the supportive arene C-H…nitro interaction (b) that link adjacent zig-zag hydrogen-bonded strands of 1



Scheme 4 Bifurcated C-H…O (nitro) interaction in the structure of 4-nitrophenylacetylene



Fig. 3 Crystal packing of 2 showing the two dimensional sheet of molecules with the C-H...O hydrogen bonds a, b and c indicated

H···O angle is  $166.6(2)^{\circ}$ . The inter-strand packing is reinforced with close benzene C–H···O interactions b and c shown in Fig. 2 with H1···O2 and H5···O1 distances of 2.572(6) and 2.581(6) Å and C–H···O angles of 137.9(2) and 133.4(2)°.

The alkyne-nitro interaction here contrasts with the symmetric bifurcated interaction first reported by Philp and Harris in 1999 [11]. That interaction is best visualized in the crystal structure of 4-nitrophenylacetylene with one-dimensional linear ribbons formed through a bifurcated C–H…nitro interaction as shown in Scheme 4. The C–H…O distances of 2.318 and 2.429 Å are significantly less than the sum of the van der Waals radii of 2.72 Å and the linearity of the interaction is confirmed by the alkyne C–C…N angle of 177.32°.

The crystal packing of dimethyl analogue **2** is also dominated by C–H···O nitro interactions as shown in Fig. 3. There is a weak bifurcated alkyne-nitro C–H···O hydrogen bond between molecules **A** and **B** shown as "**a**" in Fig. 3. The H···O distances are 2.609(2) and 2.566(2) Å for O1– H18 and O2–H18 respectively with an alkyne C–H···N angle of 174.55(15)°. A symmetry related alkyne makes a second C–H···O hydrogen bond (**b** in Fig. 3) to O2 of symmetry related molecule **B**'. The H···O distance is 2.478(2) Å and the C–H···O angle is 147.15(15)°. Thus four molecules, shown as **A**, **B**, **B**' and **A**' in Fig. 3 are connected by the alkyne-nitro hydrogen bonds. This group of molecules are further linked by two symmetry related phenyl C–H···O hydrogen bonds **c**. The H···O distance is 2.429(2) Å.

#### Conclusions

In conclusion we confirm that the crystal packing of sterically congested ortho-nitro phenylacetylenes is dominated by alkyne C–H…nitro interactions supplemented by arene C–H…nitro interactions. The intramolecular interaction between the nitro moiety and the proximal alkyne most likely contributes to the enhanced rate of hydration of the alkyne under conditions that reduce nitro group but do not normally result in hydration.

## **Electronic Supplementary Material**

Full details of the crystal structure determinations in cif format are available in the online version, at doi: 10.1007/ s10870-016-0660-0, and have also been deposited with the Cambridge Crystallographic Data Centre with deposition numbers, 1483454 and 1483455 for **1** and **2**. Copies of these can be obtained free of charge on written application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033); on request by e-mail to deposit@ccdc. cam.ac.uk or by access to http://www.ccdc.cam.ac.uk

**Acknowledgments** The Missouri State University Provost Incentive Fund funded the purchase of the X-ray diffractometer.

## References

- 1. Bosch E, Jeffries L (2001) Tetrahedron Lett 42:8141
- 2. Bosch E, Unpublished results. The reduction with iron/ammonium chloride in acetic acid has been reported in a Japanese

Patent: Yamakawa K, Sato T JP 10036325 (Chem. Abstr. 128:167247)

- Pilkington M, Wallis JD, Smith GT, Howard JAK (1996) J Chem Soc Perkin Trans 2:1849–1854
- 4. Bruker (2014) SMART and SAINT. Bruker AXS Inc., Madison
- 5. Sheldrick GM (2015) Acta Cryst Sect C Struct Chem C71:3-8
- 6. Barbour LJ (2001) J Supramol Chem 1:189-191
- 7. Bondi A (1964) J Phys Chem 68:441
- Groom CR, Bruno IJ, Lightfoot MP, Ward SC (2016) The Cambridge Structural Database. Acta Cryst Sect B Struct Sci Cryst Eng Mater B72:171–179
- 9. CCDC refcodes: BOBDED, CICNEJ, SOLHUX, SUVLIE, TOHXAP, TOHXAP01, UKICAS, VASKEG, VASKIK, VASOQ, WAGKEU, ZIBHUP
- Zeng X, Wang C, Batsanov AS, Bryce MR, Gigon J, Urasinska-Wojcik B, Ashwell GJ (2010) J Org Chem 75:130–136
- 11. Robinson JMA, Philp D, Harris KDM (1999) Chem Commun 329–300