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### (E)- and (Z)-4-Ethynyl-4'-nitrostilbene

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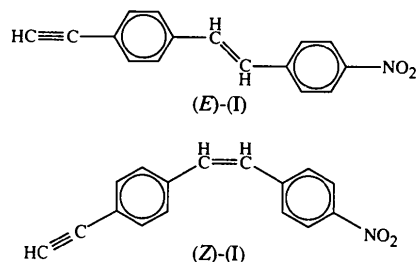
#### Abstract

Structural determinations of the *E* and *Z* isomers of 4-ethynyl-4'-nitrostilbene, C<sub>12</sub>H<sub>11</sub>NO<sub>2</sub>, have been carried out, the first such studies of 'extended-chain' acetylenes bearing the prototypical NO<sub>2</sub> acceptor group.

#### Comment

We have been investigating the non-linear optical merit of organometallic complexes (Whittall *et al.*, 1994; Whittall, Humphrey, Hockless, Skelton & White, 1995; Whittall, Humphrey, Samoc, Swiatkiewicz & Luther-Davies, 1995; Whittall, Humphrey, Persoons & Houbrechts, 1996; McDonagh, Whittall, Humphrey, Skelton & White, 1995; McDonagh *et al.*, 1996). Our utilization of the semi-empirical routine *ZINDO* (Biosym Technologies, 1994) has necessitated access to accurate molecular geometries for metal complexes and ligand fragments. We report herein the structural determinations of both the *Z* and *E* isomers of 4-ethynyl-4'-nitrostilbene, (I), which can be readily incorporated into (cyclopentadienyl)bis(phosphine)ruthenium and *trans*-chlorobis(diphosphine)ruthenium environments as the corresponding acetylide ligands (Whittall *et al.*, 1995; McDonagh *et al.*, 1995, 1996). These are the first struc-

tural studies of 'extended-chain' acetylenes bearing the prototypical NO<sub>2</sub> acceptor group.



The formation of the two isomers of 4-HC<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-CH=CHC<sub>6</sub>H<sub>4</sub>-4'-NO<sub>2</sub> was carried out by coupling 4-ethynylbenzaldehyde and 4-nitrobenzyltriphenylphosphonium bromide according to standard Wittig methods. The structural studies (Fig. 1) show no significant differences in bond length and angle parameters other than those associated with the differing geometries about the alkene linkage [C(6)—C(15)—C(16) 131.5 (2)° (*Z*) and 127.3 (2)° (*E*); C(15)—C(16)—C(9) 131.8 (2)° (*Z*) and 124.1 (2)° (*E*)], readily explicable from phenyl-phenyl repulsion in the *Z* isomer.

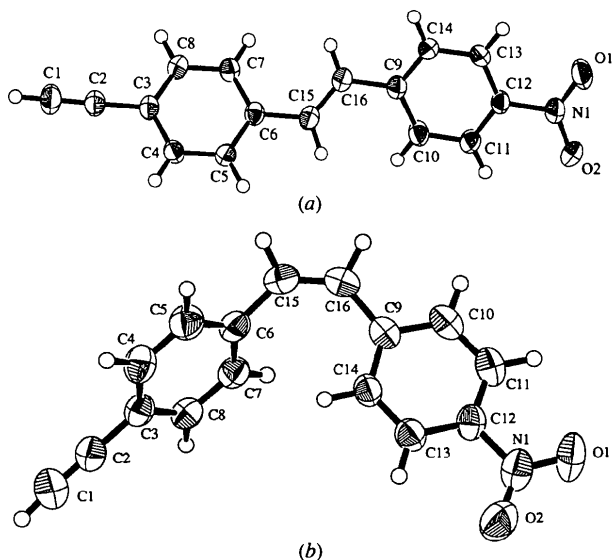


Fig. 1. The molecular structures of (a) (*E*)-4-ethynyl-4'-nitrostilbene and (b) (*Z*)-4-ethynyl-4'-nitrostilbene, showing the labelling schemes for the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as circles of arbitrary radii.

#### Experimental

The title isomeric compounds were synthesized by reacting molar equivalents of 4-ethynylbenzaldehyde and 4-nitrobenzyltriphenylphosphonium bromide in methanol. A solution of sodium methoxide in methanol was added and the mixture stirred for 2 h and then cooled in ice. The resulting mixture

was then filtered to afford a yellow powder of (*E*)-4- $\text{HC}_2\text{C}_6\text{H}_4\text{-CH=CHC}_6\text{H}_4\text{-4}'\text{-NO}_2$  (22%). Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated  $\text{CHCl}_3$  solution. The filtrate was concentrated and then filtered to afford (*Z*)-4- $\text{HC}_2\text{C}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{-4}'\text{-NO}_2$  (54%). Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated methanol solution.

***E* isomer***Crystal data* $\text{C}_{16}\text{H}_{11}\text{NO}_2$  $M_r = 249.27$ 

Monoclinic

 $P2_1/n$  $a = 6.853$  (2) Å $b = 17.675$  (2) Å $c = 10.203$  (2) Å $\beta = 92.37$  (2)° $V = 1234.9$  (3) Å<sup>3</sup> $Z = 4$  $D_x = 1.341$  Mg m<sup>-3</sup> $D_m$  not measured*Data collection*

Rigaku AFC-6R diffractometer

 $\omega/2\theta$  scans

Absorption correction:

 $\psi$  scans (North, Phillips & Mathews, 1968) $T_{\min} = 0.962$ ,  $T_{\max} = 1.000$ 

2092 measured reflections

1918 independent reflections

*Refinement*Refinement on  $F^2$  $R = 0.0358$  $wR = 0.0386$  $S = 2.857$ 

1533 reflections

217 parameters

All H-atom parameters refined

 $w = 4F_o^2/[\sigma^2(F_o^2) + (0.009F_o^2)^2]$  $(\Delta/\sigma)_{\max} = 0.0003$ Cu  $K\alpha$  radiation $\lambda = 1.5418$  Å

Cell parameters from 25 reflections

 $\theta = 46.9\text{--}49.9^\circ$  $\mu = 0.722$  mm<sup>-1</sup> $T = 213$  (1) K

Prism

 $0.36 \times 0.16 \times 0.14$  mm

Pale yellow

1533 observed reflections

 $[I > 3\sigma(I)]$  $R_{\text{int}} = 0.0353$  $\theta_{\text{max}} = 60.04^\circ$  $h = 0 \rightarrow 7$  $k = 0 \rightarrow 19$  $l = -11 \rightarrow 11$ 

3 standard reflections

monitored every 150

reflections

intensity decay: none

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for the *E* isomer of (*I*)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	-0.2899 (2)	0.17555 (9)	1.3090 (2)	0.0640 (5)
O(2)	-0.2964 (2)	0.05697 (9)	1.2617 (1)	0.0585 (5)
N(1)	-0.2226 (2)	0.11992 (10)	1.2553 (2)	0.0417 (5)
C(1)	1.2934 (3)	0.1331 (1)	0.4667 (2)	0.0541 (7)
C(2)	1.1649 (3)	0.1261 (1)	0.5384 (2)	0.0404 (6)
C(3)	1.0042 (3)	0.1188 (1)	0.6251 (2)	0.0338 (5)

C(4)	0.8451 (3)	0.0729 (1)	0.5918 (2)	0.0373 (6)
C(5)	0.6883 (3)	0.0685 (1)	0.6730 (2)	0.0364 (6)
C(6)	0.6849 (3)	0.1109 (1)	0.7884 (2)	0.0326 (5)
C(7)	0.8468 (3)	0.1556 (1)	0.8223 (2)	0.0354 (6)
C(8)	1.0042 (3)	0.1594 (1)	0.7420 (2)	0.0363 (6)
C(9)	0.2883 (3)	0.1451 (1)	1.0407 (2)	0.0331 (5)
C(10)	0.2127 (3)	0.0734 (1)	1.0668 (2)	0.0394 (6)
C(11)	0.0461 (3)	0.0649 (1)	1.1367 (2)	0.0384 (6)
C(12)	-0.0454 (3)	0.1290 (1)	1.1816 (2)	0.0330 (5)
C(13)	0.0260 (3)	0.2007 (1)	1.1607 (2)	0.0366 (6)
C(14)	0.1929 (3)	0.2083 (1)	1.0896 (2)	0.0365 (6)
C(15)	0.5143 (3)	0.1058 (1)	0.8704 (2)	0.0355 (6)
C(16)	0.4617 (3)	0.1542 (1)	0.9621 (2)	0.0362 (6)

Table 2. Selected geometric parameters (Å, °) for the *E* isomer of (*I*)

O(1)—N(1)	1.225 (2)	C(6)—C(15)	1.469 (3)
O(2)—N(1)	1.224 (2)	C(7)—C(8)	1.383 (3)
N(1)—C(12)	1.465 (2)	C(9)—C(10)	1.397 (3)
C(1)—C(2)	1.175 (3)	C(9)—C(14)	1.398 (3)
C(2)—C(3)	1.447 (3)	C(9)—C(16)	1.470 (3)
C(3)—C(4)	1.389 (3)	C(10)—C(11)	1.380 (3)
C(3)—C(8)	1.391 (3)	C(11)—C(12)	1.382 (3)
C(4)—C(5)	1.387 (3)	C(12)—C(13)	1.377 (3)
C(5)—C(6)	1.396 (3)	C(13)—C(14)	1.387 (3)
C(6)—C(7)	1.394 (3)	C(15)—C(16)	1.329 (3)
O(1)—N(1)—O(2)	122.9 (2)	C(3)—C(8)—C(7)	120.7 (2)
O(1)—N(1)—C(12)	118.4 (2)	C(10)—C(9)—C(14)	118.3 (2)
O(2)—N(1)—C(12)	118.7 (2)	C(10)—C(9)—C(16)	121.2 (2)
C(1)—C(2)—C(3)	178.7 (2)	C(14)—C(9)—C(16)	120.4 (2)
C(2)—C(3)—C(4)	120.8 (2)	C(9)—C(10)—C(11)	121.3 (2)
C(2)—C(3)—C(8)	120.3 (2)	C(10)—C(11)—C(12)	118.5 (2)
C(4)—C(3)—C(8)	118.9 (2)	N(1)—C(12)—C(11)	118.5 (2)
C(3)—C(4)—C(5)	120.4 (2)	N(1)—C(12)—C(13)	119.2 (2)
C(4)—C(5)—C(6)	120.9 (2)	C(11)—C(12)—C(13)	122.3 (2)
C(5)—C(6)—C(7)	118.2 (2)	C(12)—C(13)—C(14)	118.5 (2)
C(5)—C(6)—C(15)	119.2 (2)	C(9)—C(14)—C(13)	121.1 (2)
C(7)—C(6)—C(15)	122.5 (2)	C(6)—C(15)—C(16)	127.3 (2)
C(6)—C(7)—C(8)	120.8 (2)	C(9)—C(16)—C(15)	124.1 (2)

***Z* isomer***Crystal data* $\text{C}_{16}\text{H}_{11}\text{NO}_2$  $M_r = 249.27$ 

Monoclinic

 $P2_1/a$  $a = 10.027$  (1) Å $b = 11.037$  (2) Å $c = 12.472$  (1) Å $\beta = 112.015$  (9)° $V = 1279.6$  (3) Å<sup>3</sup> $Z = 4$  $D_x = 1.294$  Mg m<sup>-3</sup> $D_m$  not measured*Data collection*

Rigaku AFC-6R diffractometer

 $\omega/2\theta$  scans

Absorption correction:

 $\psi$  scans (North, Phillips & Mathews, 1968) $T_{\min} = 0.973$ ,  $T_{\max} = 1.000$ 

2144 measured reflections

2019 independent reflections

Cu  $K\alpha$  radiation $\lambda = 1.5418$  Å

Cell parameters from 25

reflections

 $\theta = 46.0\text{--}49.2^\circ$  $\mu = 0.658$  mm<sup>-1</sup> $T = 296$  (1) K

Prism

 $0.46 \times 0.16 \times 0.13$  mm

Yellow

1483 observed reflections

 $[I > 3\sigma(I)]$  $R_{\text{int}} = 0.0339$  $\theta_{\text{max}} = 60.04^\circ$  $h = 0 \rightarrow 11$  $k = 0 \rightarrow 12$  $l = -14 \rightarrow 12$ 

3 standard reflections

monitored every 150

reflections

intensity decay: none

## Refinement

Refinement on *F**R* = 0.0377*wR* = 0.0400*S* = 2.876

1483 reflections

217 parameters

All H-atom parameters

refined

 $w = 4F_o^2 / [\sigma^2(F_o^2) + (0.007F_o^2)^2]$  $(\Delta/\sigma)_{\max} = 0.0001$  $\Delta\rho_{\max} = 0.13 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.13 \text{ e } \text{\AA}^{-3}$ 

Extinction correction:

Zachariasen (1967) type

2, Gaussian isotropic

Extinction coefficient:

 $1.24(4) \times 10^{-5}$ 

Atomic scattering factors

from *International Tables*for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

The  $\theta$ -scan widths used were  $(1.20 + 0.3\tan\theta)^\circ$  at speeds of 16 and  $32^\circ \text{ min}^{-1}$  (in  $\omega$ ) for the *E* and *Z* isomers, respectively. The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak-to-background counting time. H atoms were located from difference maps and allowed to refine. All non-H atoms were refined anisotropically in both cases. The structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1995).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN*; program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994) and *DIRDIF94* (Beurskens *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for the *Z* isomer of (*I*)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O(1)	0.7801 (2)	-0.1640 (2)	0.5044 (2)	0.0883 (8)
O(2)	0.6370 (2)	-0.2927 (2)	0.5346 (2)	0.1016 (9)
N(1)	0.6889 (2)	-0.1913 (2)	0.5434 (2)	0.0671 (8)
C(1)	-0.1103 (3)	-0.2088 (3)	0.8619 (3)	0.0718 (10)
C(2)	-0.0219 (3)	-0.1435 (2)	0.8559 (2)	0.0568 (8)
C(3)	0.0889 (2)	-0.0635 (2)	0.8508 (2)	0.0506 (7)
C(4)	0.1902 (3)	-0.0164 (3)	0.9517 (2)	0.0640 (9)
C(5)	0.2981 (3)	0.0599 (3)	0.9477 (2)	0.0622 (8)
C(6)	0.3103 (2)	0.0882 (2)	0.8433 (2)	0.0513 (7)
C(7)	0.2080 (3)	0.0417 (2)	0.7425 (2)	0.0513 (7)
C(8)	0.0987 (3)	-0.0327 (2)	0.7456 (2)	0.0507 (7)
C(9)	0.5518 (2)	0.0750 (2)	0.7235 (2)	0.0496 (7)
C(10)	0.6423 (3)	0.1042 (2)	0.6654 (2)	0.0587 (8)
C(11)	0.6876 (3)	0.0186 (3)	0.6060 (2)	0.0583 (8)
C(12)	0.6401 (2)	-0.0981 (2)	0.6046 (2)	0.0514 (7)
C(13)	0.5502 (3)	-0.1316 (2)	0.6599 (2)	0.0544 (8)
C(14)	0.5074 (3)	-0.0452 (2)	0.7200 (2)	0.0517 (7)
C(15)	0.4222 (3)	0.1748 (2)	0.8423 (2)	0.0616 (8)
C(16)	0.5155 (3)	0.1711 (2)	0.7901 (2)	0.0604 (8)

Table 4. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for the *Z* isomer of (*I*)

O(1)—N(1)	1.223 (2)	C(6)—C(15)	1.477 (3)
O(2)—N(1)	1.222 (3)	C(7)—C(8)	1.382 (3)
N(1)—C(12)	1.470 (3)	C(9)—C(10)	1.394 (3)
C(1)—C(2)	1.166 (3)	C(9)—C(14)	1.395 (3)
C(2)—C(3)	1.439 (3)	C(9)—C(16)	1.474 (3)
C(3)—C(4)	1.389 (3)	C(10)—C(11)	1.379 (3)
C(3)—C(8)	1.393 (3)	C(11)—C(12)	1.372 (3)
C(4)—C(5)	1.387 (3)	C(12)—C(13)	1.376 (3)
C(5)—C(6)	1.388 (3)	C(13)—C(14)	1.377 (3)
C(6)—C(7)	1.389 (3)	C(15)—C(16)	1.326 (3)
O(1)—N(1)—O(2)	123.1 (2)	C(3)—C(8)—C(7)	120.6 (2)
O(1)—N(1)—C(12)	118.6 (2)	C(10)—C(9)—C(14)	117.7 (2)
O(2)—N(1)—C(12)	118.3 (2)	C(10)—C(9)—C(16)	118.2 (2)
C(1)—C(2)—C(3)	178.9 (3)	C(14)—C(9)—C(16)	124.0 (2)
C(2)—C(3)—C(4)	120.3 (2)	C(9)—C(10)—C(11)	122.1 (2)
C(2)—C(3)—C(8)	121.3 (2)	C(10)—C(11)—C(12)	117.9 (2)
C(4)—C(3)—C(8)	118.4 (2)	N(1)—C(12)—C(11)	118.8 (2)
C(3)—C(4)—C(5)	120.7 (2)	N(1)—C(12)—C(13)	118.8 (2)
C(4)—C(5)—C(6)	121.0 (2)	C(11)—C(12)—C(13)	122.4 (2)
C(5)—C(6)—C(7)	118.1 (2)	C(12)—C(13)—C(14)	118.9 (2)
C(5)—C(6)—C(15)	119.2 (2)	C(9)—C(14)—C(13)	121.0 (2)
C(7)—C(6)—C(15)	122.5 (2)	C(6)—C(15)—C(16)	131.5 (2)
C(6)—C(7)—C(8)	121.2 (2)	C(9)—C(16)—C(15)	131.8 (2)

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1091). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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