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Acta Cryst. (1996). C**52**, 3222–3224

(*E*)- and (*Z*)-4-Ethynyl-4′-nitrostilbene

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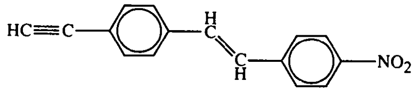
(*Received 22 February 1996; accepted 22 July 1996*)

Abstract

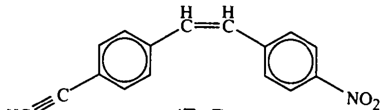
Structural determinations of the *E* and *Z* isomers of 4-ethynyl-4′-nitrostilbene, $C_{16}H_{11}NO_2$, have been carried out, the first such studies of 'extended-chain' acetylenes bearing the prototypical NO_2 acceptor group.

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 structural studies of 'extended-chain' acetylenes bearing the prototypical NO_2 acceptor group.



(*E*)-(I)



(*Z*)-(I)

The formation of the two isomers of 4-$HC_2C_6H_4$-$CH{=}CHC_6H_4$-4′-NO_2 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.

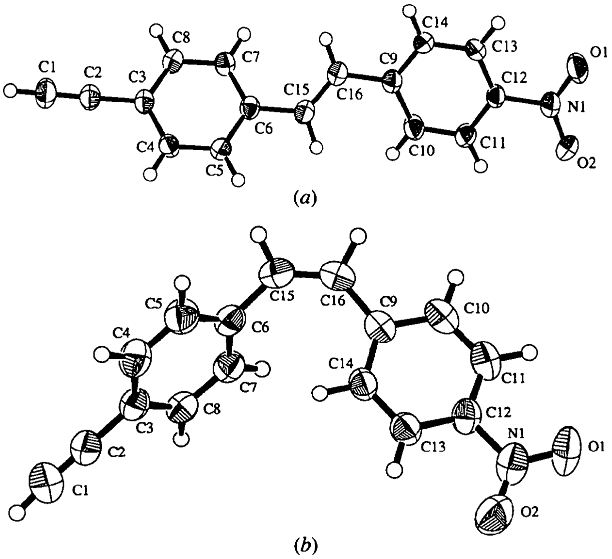


Fig. 1. The molecular structures of (*a*) (*E*)-4-ethynyl-4′-nitrostilbene and (*b*) (*Z*)-4-ethynyl-4′-nitrostilbene, showing the labelling schemes for the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as circles of arbitrary radii.

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-$HC_2C_6H_4$-$CH{=}CHC_6H_4$-4′-NO_2 (22%). Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated $CHCl_3$ solution. The filtrate was concentrated and then filtered to afford (*Z*)-4-$HC_2C_6H_4CH{=}CHC_6H_4$-4′-NO_2 (54%). Crystals suitable for diffraction analysis were grown by slow evaporation of a saturated methanol solution.

E isomer

Crystal data

$C_{16}H_{11}NO_2$
$M_r = 249.27$
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^3
$Z = 4$
$D_x = 1.341$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 46.9$–$49.9°$
$\mu = 0.722$ mm^{-1}
$T = 213\ (1)$ K
Prism
0.36 × 0.16 × 0.14 mm
Pale yellow

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.962$, $T_{\max} = 1.000$
2092 measured reflections
1918 independent reflections

1533 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.0353$
$\theta_{\max} = 60.04°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 19$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 150 reflections intensity decay: none

Refinement

Refinement on *F*
$R = 0.0358$
$wR = 0.0386$
$S = 2.857$
1533 reflections
217 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.009F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0003$

$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: $9.5\ (4) \times 10^{-6}$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
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

$C_{16}H_{11}NO_2$
$M_r = 249.27$
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^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 46.0$–$49.2°$
$\mu = 0.658$ mm^{-1}
$T = 296\ (1)$ K
Prism
0.46 × 0.16 × 0.13 mm
Yellow

Data collection

Rigaku AFC-6*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min} = 0.973$, $T_{\max} = 1.000$
2144 measured reflections
2019 independent reflections

1483 observed reflections $[I > 3\sigma(I)]$
$R_{\rm int} = 0.0339$
$\theta_{\max} = 60.04°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 12$
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
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.007F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.0001$
$\Delta\rho_{\max} = 0.13$ e Å^{-3}
$\Delta\rho_{\min} = -0.13$ e Å^{-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)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the Z isomer of (I)*

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

	x	y	z	U_{eq}
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 (Å, °) 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)

The θ-scan widths used were $(1.20 + 0.3\tan\theta)^\circ$ at speeds of 16 and 32° min^{-1} (in ω) 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: *SIR*92 (Altomare *et al.*, 1994) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

IRW holds an ARC Australian Postgraduate Research Award (Industry) and MGH holds an ARC Australian Research Fellowship. Dr A. C. Willis is thanked for the data collection for the Z isomer.

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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