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π–π-Stacking and nitro–π-stacking interactions of 1-(4-nitrophenyl)-4-phenyl-2,4-bis(phenylethynyl)butadiene

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Key indicators

Single-crystal synchrotron study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.059
wR factor = 0.156
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The first observed side product, $C_{32}H_{21}NO_2$, in the Sonogashira coupling reaction is reported. The molecular packing shows a high degree of π-stacking interactions in the solid state.

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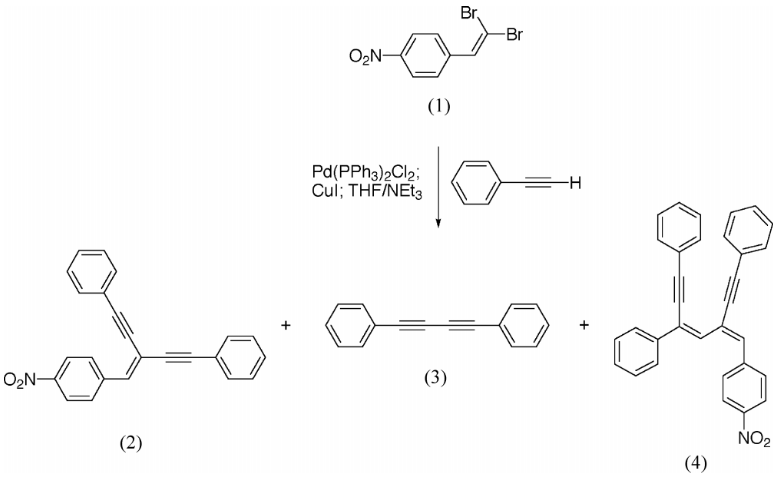
Contribution 486 from the Center for Photochemical Sciences. This paper is dedicated to Professor Dr J. W. Neckers on the occasion of his 100th birthday.

Comment

In this paper, we report the X-ray structure and stacking of 1-(4-nitrophenyl)-4-phenyl-2,4-bis(phenylethynyl)butadiene, (4). This compound was isolated as a side product during the Sonogashira (Sonogashira *et al.*, 1975) coupling reaction of β,β-dibromo-*p*-nitrostyrene, (1), and phenylacetylene to afford Y-enyne (3) (Kaafarani & Neckers, 2001; Kaafarani *et al.*, 2001; Kaafarani, Wex, Krause Bauer & Neckers, 2002; Kaafarani, Wex, Strehmer & Neckers, 2002). A diyne, formed by reductive elimination, is a classical side product in the course of the Sonogashira coupling reaction [in this case, 1,4-diphenylbutadiyne (3)] (Nicolaou & Sorensen, 1996). It appears to us that compound (4) is formed after the addition of another phenylacetylene to Y-enyne (2). To the best of our knowledge, this is the first report of such a side product in the Sonogashira coupling reaction.



The molecular structure of (4) is shown in Fig. 1. Nitro substitution has been reported to induce π–π-stacking interactions (Garden *et al.*, 2002). The nitro-substitution-induced π–π-stacking and nitro–π-stacking interactions in (4) are shown in Fig. 2. The distance between the centroids of the phenyl rings alternates between 4.96 and 5.35 Å. The distance between the centers of the acetylene triple bonds is 3.28 Å. The strong electron-withdrawing NO_2 group interacts with the π-system of the phenyl ring of a neighboring molecule. The distance between the N atom and the center of the phenyl rings varies between 3.58 and 5.08 Å for the alternating layers

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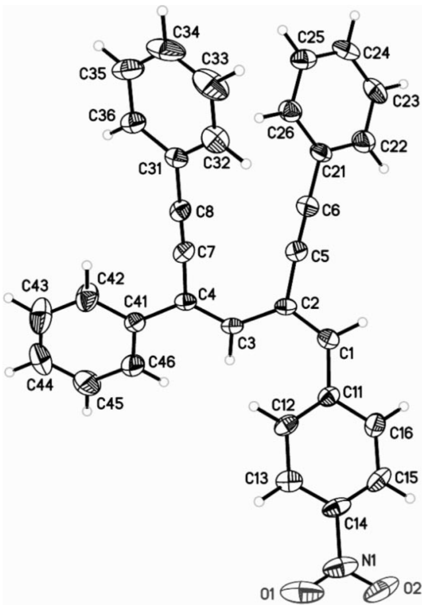


Figure 1
The structure of (4) at 173 K, showing the atomic labelling and 50% probability ellipsoids.

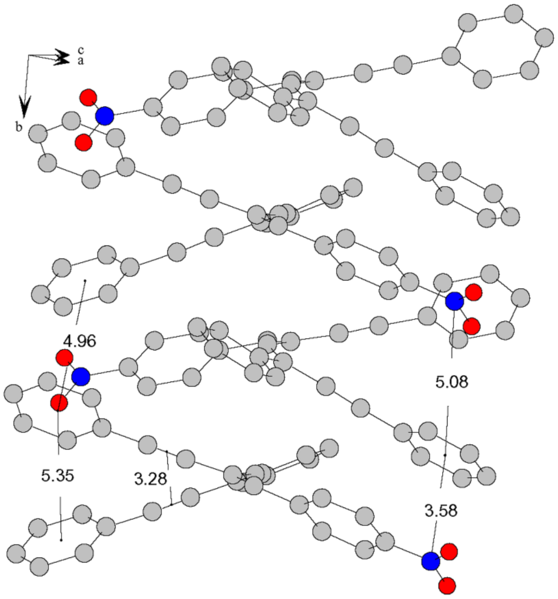


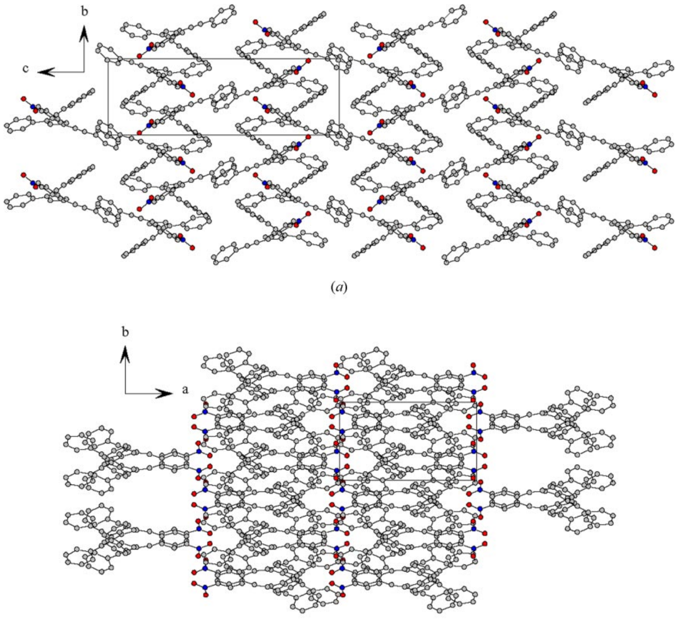
Figure 2
π–π–Stacking and nitro–π interactions of (4).

(Fig. 2). The molecular packing of (4) is shown in Fig. 3.

The scanning electron micrograph (SEM) of (4) shows its crystal habit in the form of complex, cactus-like needles with a diameter of several micrometers (Fig. 4). Interestingly, these tubes seem hollow; however, a shadow effect induced by the restricted lateral placement of the detector in the SEM can not be excluded and further analysis will be required to confirm this observation.

Experimental

Single crystals were obtained from methanol–methylene chloride solutions. Due to the weakly diffracting nature of the sample and the small crystal size, it was necessary to collect data using synchrotron radiation rather than a laboratory source. A suitable crystal was mounted on the tip of a glass fiber with paratone-N and immediately transferred to the goniostat bathed in a cold stream.



(*a*)

(*b*)

Figure 3
The molecular packing of (4), viewed (*a*) in the *bc* plane and (*b*) in the *ab* plane.

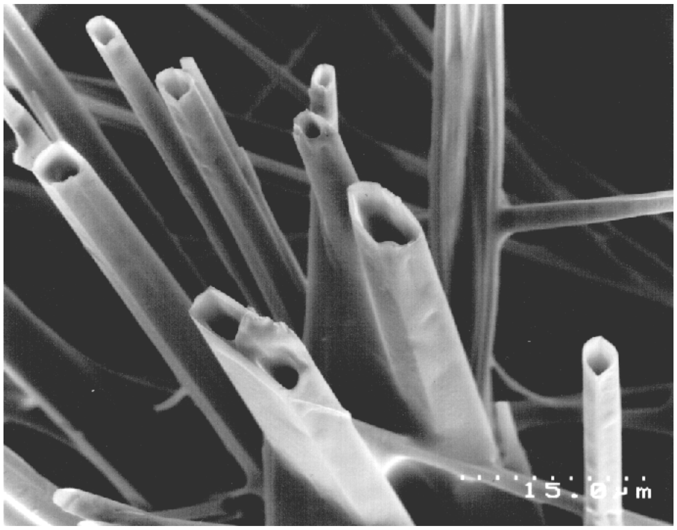


Figure 4
An SEM micrograph of (4).

Crystal data

$C_{32}H_{21}NO_2$
$M_r = 451.50$
Monoclinic, $P2_1/c$
$a = 13.583$ (3) Å
$b = 7.6515$ (14) Å
$c = 23.399$ (5) Å
$\beta = 100.093$ (11)°
$V = 2394.2$ (9) Å^3
$Z = 4$
$D_x = 1.253$ Mg m^{-3}

Synchrotron radiation
$\lambda = 0.885$ Å
Cell parameters from 4292 reflections
$\theta = 6.9$–29.0°
$\mu = 0.08$ mm^{-1}
$T = 173$ (2) K
Needle, orange
0.07 × 0.06 × 0.05 mm

Data collection

Bruker Proteum300 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min} = 0.995$, $T_{\max} = 0.996$
19213 measured reflections
3438 independent reflections

2579 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.095$
$\theta_{\max} = 29.5°$
$h = -15 \rightarrow 15$
$k = -7 \rightarrow 8$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.156$
$S = 1.07$
3438 reflections
316 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + 0.5111P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—N1	1.224 (3)	C3—C4	1.348 (3)
O2—N1	1.227 (3)	C4—C7	1.436 (3)
N1—C14	1.461 (3)	C4—C41	1.473 (4)
C1—C2	1.354 (3)	C5—C6	1.193 (3)
C1—C11	1.454 (3)	C6—C21	1.436 (4)
C2—C5	1.437 (4)	C7—C8	1.192 (3)
C2—C3	1.449 (4)	C8—C31	1.431 (3)
O1—N1—O2	124.3 (3)	C4—C3—C2	128.6 (2)
O1—N1—C14	117.7 (3)	C3—C4—C7	119.9 (2)
O2—N1—C14	118.0 (3)	C6—C5—C2	176.8 (3)
C2—C1—C11	128.3 (3)	C5—C6—C21	179.5 (3)
C1—C2—C5	116.8 (2)	C8—C7—C4	176.8 (3)
C1—C2—C3	123.3 (2)	C7—C8—C31	176.7 (2)
C5—C2—C3	119.6 (2)		

Intensity data were collected at 173 K, using a Proteum300 detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory). The detector was set at a distance of 6.6 cm from the crystal. A series of 1 s data frames measured at 0.2° increments of ω were collected to calculate a unit cell and to measure a hemisphere of intensity data. Data were corrected for absorption using *SADABS* (6, 1 harmonics) and a high resolution limit of 0.85 Å applied, based on examination of the final merged listing from *SAINT*. A high $|I - \langle I \rangle|$ error was also applied (10 s.u.) to remove outliers from the data set.

All H atoms were included in calculated geometries (C—H = 0.95 Å), riding on the parent atom. The isotropic displacement parameters for the H atoms were set as $1.2U_{\rm eq}$ of the adjacent atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *DIAMOND* (Crystal Impact, 1997); software used to prepare material for publication: *SHELXTL*.

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