(E)-1-(4-Methylphenyl)-2-(4-nitrophenyl)ethene

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Key indicators

Single-crystal X-ray study
$T = 291$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.052
wR factor = 0.184
Data-to-parameter ratio = 10.7

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

The title compound, $C_{15}H_{13}NO_2$, is a stilbene derivative with a push–pull conjugated system. The molecules form sheets with a head-to-tail arrangement both within and between the sheets.

Comment

The title compound, (I), was synthesized as a precursor for longer poly(p-phenylenevinylene) oligomers with non-linear optical properties (Cheng, Tam, Stevenson *et al.*, 1991; Cheng, Tam, Marder *et al.*, 1991), and for use in organic memories (Bandyopadhyay & Pal, 2003). It was recently shown to be highly mutagenic (Ludolph *et al.*, 2001).

(I)
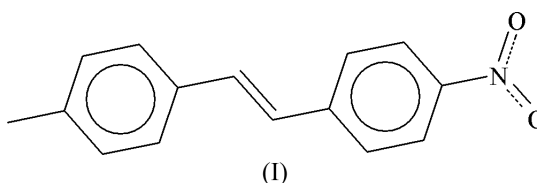
Once corrected for libration effects, the differences in the intramolecular distances and angles are as expected for a room temperature measurement of an (E)-stilbene. For a discussion on the bond lengths and angles in and around the ethenylic bond, see Ogawa *et al.* (1992). The methyl-substituted ring B is slightly larger than the nitro-substituted ring A (Fig. 1), with the longest aromatic bonds involving C1 and C11, which are connected to the ethenylic link.

By itself, the molecule is a push–pull conjugated system and therefore it comes as no surprise that the compound crystallizes in the space group $P\bar{1}$, with the dipoles arranged head-to-tail within and between sheets, as is clearly demonstrated in Fig. 2. These stacks of alternating dipoles also give rise to π-stacking interactions, given by $CgA \cdots CgB^i = 3.920$ (3) Å, 26.86° and perp = 3.497 Å, and $CgA \cdots CgB^{ii} = 3.898$ (3) Å, 25.66° and perp = 3.514 Å, in which Cg is the centroid of the
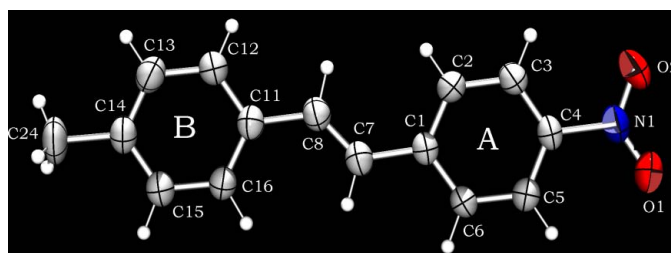
Figure 1
View of (I), with the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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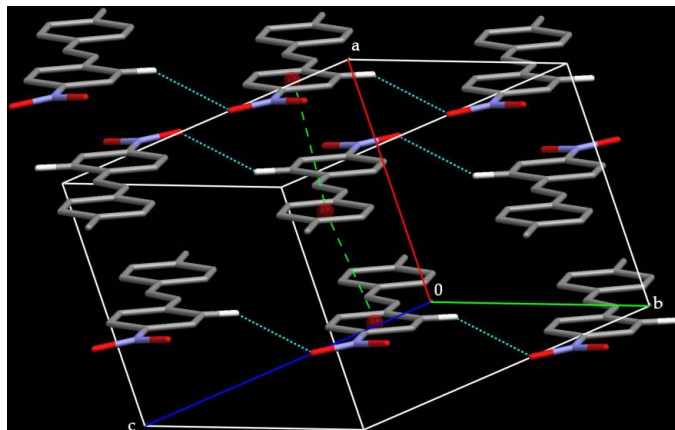
Figure 2
View of the packing of (I). H atoms have been omitted unless these are involved in hydrogen bonding. The π-stacking interactions are indicated by dashed lines and C—H···O hydrogen bonds are indicated by dotted lines.

ring, the angle is relative to the normal of the plane of ring A, and the distance indicated by 'perp' is the perpendicular distance between CgB and the least-squares plane of ring A [symmetry codes: (i) $1 - x$, $1 - y$, $1 - z$; (ii) $2 - x$, $1 - y$, $1 - z$]. Only one intermolecular distance is shorter than the sum of the van der Waals radii, in this case by 0.18 Å, *viz.* H6···O2^{iii} [symmetry code: (iii) x, $y - 1$, z; Table 2]. The interaction links the molecules in infinite chains along the b axis, the direction in which no head-to-tail arrangement for the dipoles is possible due to the space-group symmetry. These two interactions are indicated in Fig. 2.

A TLS analysis with the program *THMA14* (Schomaker & Trueblood, 1998) indicates that the librational component $L1$, which coincides with the long axis of the molecule within 2.6°, is an order of magnitude larger than the two other ones ($L1 = 39.27°^2$, $L2 = 4.33°^2$ and $L3 = 2.78°^2$), while T and S are close to zero, as can be expected for a centrosymmetric structure.

Experimental

Compound (I) (Pfeiffer, 1915, 1916) was synthesized starting from triphenyl(*p*-xylyl)phosphonium chloride, (II), which was obtained by reacting α-chloro-*p*-xylene with triphenylphosphine in acetonitrile. Sodium (2.3 g, 0.1 mol) in dry ethanol (80 ml) was added dropwise to a stirred mixture of (II) (38.8 g, 0.1 mol) and *p*-nitrobenzaldehyde (15.1 g, 0.1 mol) in dry ethanol. The mixture was refluxed under nitrogen for 3 h. After cooling to room temperature, water (150 ml) was added to the reaction mixture and the precipitate filtered off. The yellow product was collected and redissolved in hot acetone (250 ml). This solution was poured into water (150 ml). The compound was then again collected by filtration. In order to obtain the E isomer, the compound was refluxed in toluene with a catalytic amount of iodine for 4 h. After cooling, prism-shaped crystals of (I) formed in the solution [yield 55%, m.p. (uncorrected) 422 K]. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 2.38 (*s*, 3H, H24), 7.08 (*d*, 1H, *J* = 16.33 Hz, H7), 7.20 (*d*, 2H, *J* = 8.09 Hz, H13 and H15), 7.24 (*d*, 1H, *J* = 16.33 Hz, H8), 7.44 (*d*, 2H, *J* = 8.24 Hz, H12 and H16), 7.61 (*d*, 2H, *J* = 8.85 Hz, H2 and H6), 8.20 (*d*, 2H, *J* = 8.85 Hz, H3 and H5), ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 21.35 (C24), 124.1 (C3—C5), 125.3 (C7), 126.7 (C2

and C6), 127.0 (C12 and C16), 129.6 (C13 and C15), 133.3 (C8), 133.5 (C11), 139 (C14), 144.1 (C6), 146.7 (C4).

Crystal data

$C_{15}H_{13}NO_2$	$Z = 2$
$M_r = 239.26$	$D_x = 1.313$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.339$ (1) Å	Cell parameters from 25
$b = 7.521$ (1) Å	reflections
$c = 12.230$ (4) Å	$\theta = 6.1–17.6°$
$\alpha = 98.66$ (2)°	$\mu = 0.09$ mm^{-1}
$\beta = 99.26$ (2)°	$T = 291$ (1) K
$\gamma = 111.13$ (1)°	Prism , yellow
$V = 605.3$ (2) Å^3	$0.26 \times 0.13 \times 0.13$ mm

Data collection

Enraf–Nonius MACH3 diffractometer	$\theta_{max} = 25.3°$
	$h = 0 \rightarrow 8$
Profiled $\omega/2\theta$ scans	$k = -9 \rightarrow 8$
Absorption correction: none	$l = -14 \rightarrow 14$
2520 measured reflections	3 standard reflections
2200 independent reflections	frequency: 60 min
1055 reflections with $I > 2\sigma(I)$	intensity decay: 2%
$R_{int} = 0.012$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0901P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.052$	$+ 0.1262P]$
$wR(F^2) = 0.184$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
2200 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
205 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C1—C6	1.389 (4)	C11—C12	1.391 (4)
C1—C2	1.392 (4)	C11—C8	1.465 (4)
C1—C7	1.471 (4)	C16—C11	1.390 (4)
C8—C7	1.312 (4)		
C2—C1—C7	122.4 (3)	C8—C7—C1	127.1 (3)
C6—C1—C7	119.4 (3)	C12—C11—C8	119.2 (3)
C7—C8—C11	128.4 (3)	C16—C11—C8	123.4 (3)
C2—C1—C7—C8	0.4 (5)	C12—C11—C8—C7	179.4 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6···O2^i	1.00 (3)	2.54 (3)	3.447 (5)	151 (2)

Symmetry code: (i) x, $y - 1$, z.

H atoms were located in difference density maps and refined freely [C—H = 0.94 (3)–0.99 (3) Å]. The methyl H atoms on C24 were constrained to give angles of 109.5° and $U_{iso}(H) = 1.5U_{eq}(C_{methyl})$, with their distances free to refine, yielding 0.90 Å.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *DREAR* (Blessing, 1987); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick,

1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999) and *PLATON* (Spek, 2003).

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