

A *cis*-stilbene derivative

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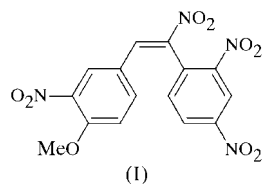
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The title compound, 4'-methoxy- $\alpha,2,3',4$ -tetranitrostilbene, C₁₅H₁₀N₄O₉, crystallizes in the centrosymmetric space group *P*2₁/*c* with one molecule in the asymmetric unit. The phenyl rings are inclined to one another and form a dihedral angle of 57.4 (1)°. The size of this angle is a result of intermolecular C—H···O interactions involving the phenyl H atoms. The torsion angle between the phenyl rings, −7.5 (3)°, indicates a *cis* geometry between them. The methoxy group is almost coplanar with the phenyl ring, and the nitro groups are twisted with respect to the phenyl rings because of the short H···O contacts. The crystal packing is stabilized by C—H···O hydrogen bonds, and the intermolecular hydrogen bonds form a *C*(12) graph-set chain running along the [010] direction.

Comment

Nitro compounds are well known for their uses as explosives, dye intermediates and battery cathodes (Sivasamy *et al.*, 1988; Renuka *et al.*, 2001). These compounds are excellent precursors for aromatic amines and medicinally important compounds. Some synthetic nitro compounds are used in perfumery. *m*-Dinitrobenzene has been found to function as



an organic cathode material in batteries. The new synthetic methodologies for polynitro compounds are of much importance in the chemical industry and defence research studies. α -Nitrostilbenes are excellent precursors for biologically active β -phenylethylamines and Michael acceptors (Robertson, 1960; Flintoft *et al.*, 1999). A survey of the literature shows that only a few styrenes undergo direct nitration to give β -nitrostyrenes, while there are no reports of side-chain nitration of stilbenes. Against this background, and in order to

obtain detailed information on the molecular conformation of nitrostilbenes in the solid state, X-ray studies of the title compound, (I), have been carried out.

Fig. 1 shows a *ZORTEP* plot (Zsolnai, 1997) of (I) with the atom-numbering scheme. Selected geometric parameters are given in Table 1. The phenyl rings are twisted out of the ethylene bond plane, as defined by the torsion angles C1—C6—C7=C8 and C7=C8—C9—C14. Therefore, the phenyl

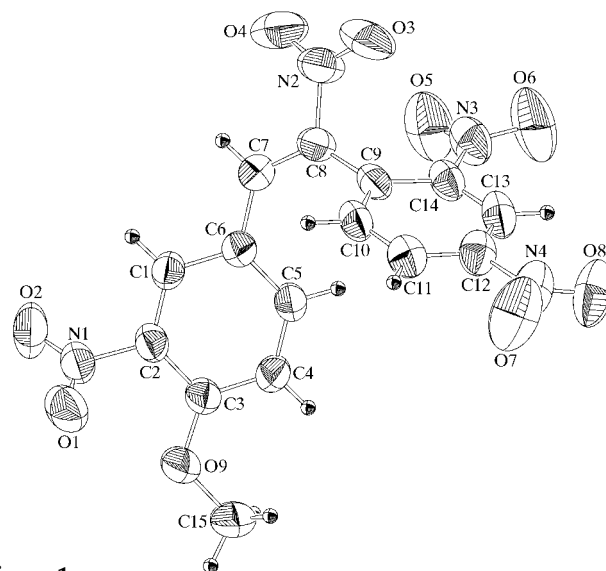


Figure 1

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

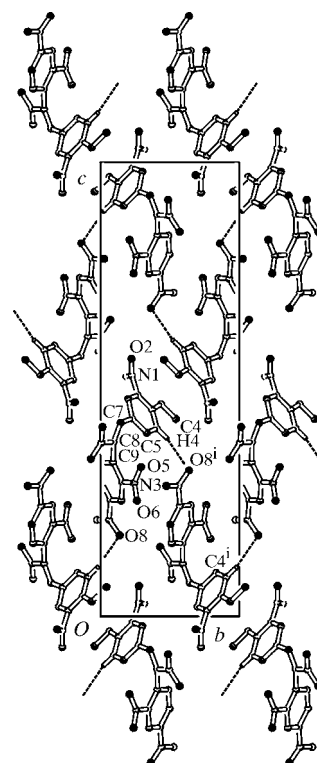


Figure 2

The crystal structure of (I), with the dashed line indicating a hydrogen bond. [Symmetry code: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

rings are inclined to each other; the dihedral angle between their mean planes is 57.4 (1)° as a result of C—H···O intermolecular interactions involving the phenyl H atoms. The bond length C7=C8 is typical both of reported ethylene C=C bond lengths [1.318 (5)–1.326 (3) Å; Finder *et al.*, 1974; Bernstein, 1975] and of a non-conjugated double bond. The N=O distances of the nitro groups, except N3=O5, are comparable to the literature $C_{ar}-NO_2$ value of 1.217 (11) Å (Allen *et al.*, 1987) and also agree with the average value of 1.216 (7) Å reported by Jeyakanthan (2000). Comparing the C7=C8 distance with the expected value of 1.317 (13) Å for a localized double bond (Allen *et al.*, 1987), it seems that there is a tendency to have some lengthening that is indicative of some π conjugation of the two phenyl rings through the central ethene bridge and agrees with the shortening of the C6—C7 and C8—C9 bonds, whose average distance, 1.471 (4), coincides with the value of 1.470 (15) Å given by Allen *et al.* (1987) for a $C_{ar}-Csp^2$ conjugate bond. Similar values have been observed for (*Z*)-5-(methoxymethyl)-3-[4-(phenylethenyl)-phenyl]-2-oxazolidinone (Durant *et al.*, 1982).

Because of the high electron-withdrawing capacity of the two NO₂ groups, the dinitrophenyl ring causes high polarization of the olefinic double bond and enhanced electron density on the carbon α to the dinitrophenyl group. This mechanism is responsible for nitration on that carbon only. The valence angles between the olefinic double bond and the two phenyl rings [C7=C8—C9 = 127.8 (2)° and C6—C7=C8 = 126.2 (2)°] are almost equal and are larger than 120°, thus indicating steric repulsion between the two aromatic rings, which are in a *cis* configuration. These values are comparable to those reported for other *cis*-stilbenes (Tinant *et al.*, 1989, 1983). The methoxy group has an almost coplanar orientation with respect to atoms C2 and C4, as is evident from the torsion angles C2—C3—O9—C15 and C4—C3—O9—C15, respectively.

Nitro group O4/N2/O3 has an almost coplanar orientation with respect to the side chain C6—C7=C8—C9, as is evident from the torsion angles O3=N2—C8=C7 and O4=N2—C8=C7. The dihedral angle between the C9—C14 and O5/N3/O6 planes is 19.9 (1)° and that between the C1—C6 and O1/N1/O2 planes is 48.1 (1)°. These nitro groups are twisted out of the plane passing through the phenyl rings to which they are attached, whereas nitro group O7/N4/O8 is nearly coplanar with C9—C14 [dihedral angle = 9.5 (1)°]. The twistings of the nitro groups are evidenced by the following short H···O contacts: H1···O2 = 2.60, H7···O4 = 2.32, H13···O6 = 2.41, H13···O8 = 2.44 and H11···O7 = 2.44 Å. Atoms C7 and C8 deviate from the planes of their attached phenyl rings by 0.094 (2) and 0.025 (2) Å, respectively. The torsion angle between the phenyl rings [C6—C7=C8—C9 = -7.5 (3)°] also indicates a *cis* geometry between them.

In addition to van der Waals interactions, the crystal packing is stabilized by C—H···O interactions (Table 2). The C4—H4···O8 hydrogen bond forms a *C*(12) graph-set chain (Bernstein *et al.*, 1995) in a zigzag manner represented by C4—H4···O8=N4—C12—C13—C14—C9—C8=C7—C6—C5, running along the [010] direction (Fig. 2).

Experimental

Fuming nitric acid (5.5 ml) was added slowly with stirring to 4'-methoxy-2,4-dinitrostilbene (1.80 g, 5 mmol). The reaction mixture was kept at 363 K for 5 min. After cooling to 298–303 K, the reaction mixture was poured over crushed ice. The crude product was filtered off, washed with water, desiccated over anhydrous CaCl₂ and recrystallized from acetone (Saravanan & Srinivasan, 2003).

Crystal data

| | |
|----------------------------------|-------------------------------------|
| $C_{15}H_{10}N_4O_9$ | $D_x = 1.521 \text{ Mg m}^{-3}$ |
| $M_r = 390.27$ | Cu $K\alpha$ radiation |
| Monoclinic, $P2_1/c$ | Cell parameters from 25 reflections |
| $a = 7.096$ (4) Å | $\theta = 5.4$ –67.9° |
| $b = 8.550$ (3) Å | $\mu = 1.12 \text{ mm}^{-1}$ |
| $c = 28.101$ (5) Å | $T = 293$ (2) K |
| $\beta = 90.87$ (3)° | Block, colourless |
| $V = 1704.7$ (12) Å ³ | 0.60 × 0.40 × 0.35 mm |
| $Z = 4$ | |

Data collection

| | |
|--|--|
| Enraf-Nonius CAD-4 diffractometer | $\theta_{\max} = 67.9^\circ$ |
| Non-profiled $\omega/2\theta$ scans | $h = 0 \rightarrow 8$ |
| 6505 measured reflections | $k = -10 \rightarrow 10$ |
| 3105 independent reflections | $l = -33 \rightarrow 33$ |
| 2787 reflections with $I > 2\sigma(I)$ | 3 standard reflections every 100 reflections |
| $R_{\text{int}} = 0.034$ | frequency: 120 min |

Refinement

| | |
|---------------------------------|---|
| Refinement on F^2 | $w = 1/[\sigma^2(F_o^2) + (0.0939P)^2 + 0.3300P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.051$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.153$ | $(\Delta/\sigma)_{\max} = 0.001$ |
| $S = 1.05$ | $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$ |
| 3105 reflections | $\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$ |
| 255 parameters | Extinction correction: <i>SHELXL</i> |
| H-atom parameters constrained | Extinction coefficient: 0.035 (2) |

Table 1

Selected geometric parameters (Å, °).

| | | | |
|--------------|-----------|--------------|-----------|
| O1—N1 | 1.226 (3) | O8—N4 | 1.213 (3) |
| O2—N1 | 1.217 (2) | O9—C3 | 1.348 (2) |
| O3—N2 | 1.223 (3) | O9—C15 | 1.430 (2) |
| O4—N2 | 1.220 (3) | C6—C7 | 1.464 (2) |
| O5—N3 | 1.184 (3) | C7—C8 | 1.327 (2) |
| O6—N3 | 1.210 (2) | C8—C9 | 1.478 (3) |
| O7—N4 | 1.210 (3) | | |
| C5—C6—C7 | 123.2 (1) | C7—C8—C9 | 127.8 (2) |
| C8—C7—C6 | 126.2 (2) | | |
| C15—O9—C3—C4 | 2.0 (3) | C1—C6—C7—C8 | 144.2 (2) |
| C2—C3—C4—C5 | 2.8 (3) | C6—C7—C8—C9 | -7.5 (3) |
| C3—C4—C5—C6 | -1.9 (3) | O4—N2—C8—C7 | -14.9 (3) |
| C2—C1—C6—C5 | 4.7 (2) | C7—C8—C9—C10 | -56.5 (2) |
| C4—C5—C6—C1 | -2.0 (3) | | |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------|-------|-------------|-------------|---------------|
| C4—H4···O8 ⁱ | 0.93 | 2.43 | 3.266 (2) | 149 |
| C15—H15B···O1 ⁱⁱ | 0.96 | 2.50 | 3.321 (3) | 144 |
| C10—H10···O2 ⁱⁱⁱ | 0.93 | 2.52 | 3.426 (3) | 164 |
| C11—H11···O3 ^{iv} | 0.93 | 2.46 | 3.226 (3) | 140 |

Symmetry codes: (i) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $x-1, y, z$.

All the H atoms were fixed geometrically and allowed to ride on their parent atoms, with C–H = 0.93–0.96 Å, and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2U_{\text{eq}}(\text{C})$ for the other H atoms.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1588). Services for accessing these data are described at the back of the journal.

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