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### 4-Methoxy-3-methyl-4'-nitrostilbene, C<sub>16</sub>H<sub>15</sub>NO<sub>3</sub>

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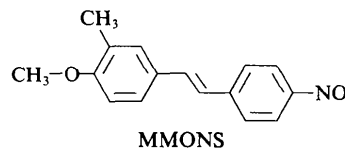
## Abstract

The molecule is planar to within 0.2 Å with a C(4)—C(7)—C(8)—C(9) torsion angle of  $-179(2)^\circ$ . The charge-transfer axis lies along the line joining the N atom at one end of the molecule to the O atom at the other. The final crystal structure is the result of complicated interplay between the short-range van der Waals interactions and the long-range dipole–

dipole interactions, making the crystal highly polarized.

## Comment

The considerable potential of organic non-linear optical materials for optical-device applications is now well established (Chemla & Zyss, 1987). 4-Methoxy-3-methyl-4'-nitrostilbene (MMONS) shows one of the largest powder second harmonic generation (SHG) signals ( $1250 \times$  urea) (Tam, Guerin, Calabrese & Stevenson, 1989; Bierlein, Cheng, Wang & Tam, 1990). It is a typical organic material in which van der Waals interactions and permanent dipole–dipole interactions are responsible for the intermolecular binding. This results in relatively low melting points and high vapour pressure. In order to understand the basic non-linear optical, thermal and mechanical properties, we carried out the X-ray structure analysis of MMONS.



MMONS was synthesized by the Wittig reaction of diethyl *p*-nitrobenzylphosphonate and 3-methyl-*p*-anisaldehyde. The product was checked and confirmed by <sup>1</sup>H NMR and high-resolution mass spectra. The material was recrystallized from methyl ethyl ketone (MEK) solution and was purified further using liquid column chromatography. The sample crystal was grown by slow evaporation of MEK at room temperature.

Fig. 1 is an ORTEP (Johnson, 1971) view of the molecule showing the atom-numbering scheme. The bond lengths O(3)—C(12) [1.351 (7) Å], O(3)—C(16) [1.413 (9) Å] and C(11)—C(15) [1.513 (10) Å] are in good agreement with the comparable bonds in 9-methoxy-11-dimethylellipticine [1.366 (4), 1.427 (7) and 1.505 (5) Å (Gansser, Viel, Mauguen & Tsoucaris, 1988)]. The mean N—O bond length of 1.22 Å for the nitro groups shows that their bond order is 1.5.

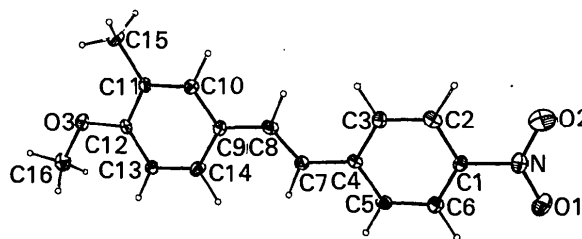


Fig. 1. Molecular structure of MMONS showing atom-numbering scheme. H atoms are drawn as circles of arbitrary radii.

The bonds connecting the two benzene rings [C(7)—C(8) = 1.315 (8), average of C(4)—C(7) and C(8)—C(9) = 1.472 Å] show double- and single-bond character, respectively. To diminish repulsions between C(7) and C(14) and between C(3) and C(8), the angles C(3)—C(4)—C(7) and C(8)—C(9)—C(14) [123.1 (6) and 123.6 (7)°, respectively] are larger than C(5)—C(4)—C(7) and C(8)—C(9)—C(10) [119.4 (6) and 118.7 (6)°, respectively]. The dihedral angle between the two phenyl rings is 5.9 (3)° and the C(4)—C(7)—C(8)—C(9) torsion angle is -179 (2)°. The stilbene moiety in MMONS is planar to within 0.15 Å, with O(1), O(2), C(15) and C(16) deviating by 0.08, -0.16, -0.16 and 0.09 Å, respectively, from the best plane. A similar planar arrangement was found in *trans*-stilbene (Hoekstra, Meertens & Vos, 1975). The nitrobenzene group in MMONS is also planar to within 0.2 Å, with a dihedral angle of 9.6 (4)° between the nitrophenyl ring and the nitro group; this conformation is comparable with those of nitrobenzene at 243 K (Trotter, 1959) and *meta*-nitroaniline (Skapski & Stevenson, 1973), which show completely planar forms.

The charge-transfer axis of the MMONS molecule lies along the line joining the N atom at one end to the O(3) atom at the other. This axis is tilted by 76, 61 and 33° from the *a*, *b* and *c* axes, respectively. The delocalization of the  $\pi$  electrons and the charge transfer from the methoxy donor group to the nitro acceptor group lead to high second-order non-linear effects. The molecules in the unit cell are orientated symmetrically about the *c* axis and therefore macroscopic polarization is established along the *c* axis.

The MMONS molecule is nearly planar and the crystal structure consists of closely spaced stacks of relatively flat molecular groups (Fig. 2). These groups lie almost parallel to the (100) planes and hence the intermolecular interactions are weakest between these planes, which were found to be the primary cleavage planes. The final structure is the result of the complicated interplay between the short-range van der Waals interactions and the long-range dipole-dipole interactions.

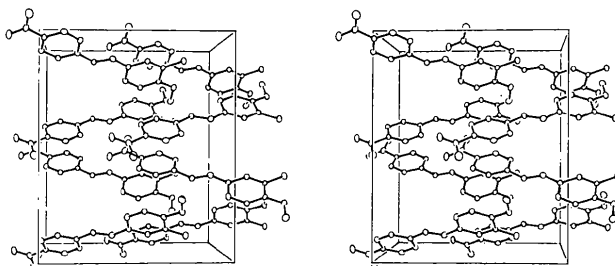


Fig. 2. A stereoview of the unit-cell packing for MMONS (*a* vertical, *c* horizontal). H atoms are omitted for clarity.

The effective value of the second-order non-linear coefficient was measured at  $\lambda = 1.06 \mu\text{m}$  and  $d_{\text{eff}} = 76 \text{ pm V}^{-1}$ . The phase matching for second harmonic generation is possible using both type I and type II conditions. MMONS has great potential utilization for highly efficient second harmonic generation.

## Experimental

### Crystal data

$\text{C}_{16}\text{H}_{15}\text{NO}_3$   
 $M_r = 269.3$   
 Orthorhombic  
*Aba2*  
 $a = 15.750 (3) \text{ \AA}$   
 $b = 13.470 (2) \text{ \AA}$   
 $c = 13.356 (2) \text{ \AA}$   
 $V = 2833 (2) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.262 \text{ Mg m}^{-3}$

Mo *K* $\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 25 reflections  
 $\theta = 10.09\text{--}14.13^\circ$   
 $\mu = 0.082 \text{ mm}^{-1}$   
 $T = 291 \text{ K}$   
 Plate  
 $0.46 \times 0.33 \times 0.30 \text{ mm}$   
 Yellow

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: none  
 1258 measured reflections  
 1221 independent reflections  
 728 observed reflections  
 $[F \geq 3\sigma(F)]$

$\theta_{\text{max}} = 25^\circ$   
 $h = 0 \rightarrow 18$   
 $k = 0 \rightarrow 15$   
 $l = 0 \rightarrow 15$   
 3 standard reflections  
 frequency: 100 min  
 intensity variation: 1.35%

### Refinement

Refinement on *F*  
 $R = 0.0414$   
 $wR = 0.0415$   
 $S = 1.067$   
 728 reflections  
 240 parameters  
 Only coordinates of H atoms refined  
 $w = 1/[\sigma^2(F) + 0.000824F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.008$   
 $\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$   
 Atomic scattering factors from SHELX76 (Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
O(1)	0.4588 (4)	-0.1941 (4)	-0.6357 (6)	0.091
O(2)	0.5353 (5)	-0.2812 (5)	-0.5342 (6)	0.106
O(3)	0.2689 (3)	0.2193 (3)	0.2064	0.064
N	0.4838 (4)	-0.2151 (6)	-0.5524 (6)	0.069
C(1)	0.4535 (4)	-0.1569 (5)	-0.4663 (8)	0.055
C(2)	0.4717 (4)	-0.1872 (5)	-0.3703 (8)	0.055
C(3)	0.4435 (4)	-0.1324 (4)	-0.2911 (6)	0.051
C(4)	0.3973 (4)	-0.0459 (4)	-0.3058 (7)	0.047
C(5)	0.3785 (6)	-0.0185 (6)	-0.4061 (7)	0.063
C(6)	0.4064 (5)	-0.0738 (6)	-0.4844 (7)	0.060
C(7)	0.3664 (5)	0.0159 (6)	-0.2235 (7)	0.056
C(8)	0.3787 (5)	0.0006 (6)	-0.1274 (7)	0.060
C(9)	0.3469 (4)	0.0616 (5)	-0.0431 (7)	0.058
C(10)	0.3711 (5)	0.0370 (6)	0.0529 (7)	0.057

C(11)	0.3472 (4)	0.0899 (5)	0.1358 (6)	0.053
C(12)	0.2928 (4)	0.1712 (5)	0.1223 (6)	0.050
C(13)	0.2665 (4)	0.1974 (5)	0.0258 (7)	0.056
C(14)	0.2938 (5)	0.1410 (5)	-0.0549 (7)	0.059
C(15)	0.3772 (7)	0.0612 (8)	0.2395 (7)	0.073
C(16)	0.2126 (6)	0.3005 (7)	0.1968 (9)	0.078

Table 2. Selected geometric parameters (Å, °)

O(1)—N	1.213 (8)	O(2)—N	1.228 (7)
O(3)—C(12)	1.351 (7)	O(3)—C(16)	1.413 (9)
N—C(1)	1.471 (9)	C(1)—C(2)	1.376 (10)
C(1)—C(6)	1.365 (10)	C(2)—C(3)	1.365 (9)
C(3)—C(4)	1.389 (8)	C(4)—C(5)	1.420 (10)
C(4)—C(7)	1.463 (9)	C(5)—C(6)	1.357 (10)
C(7)—C(8)	1.315 (8)	C(8)—C(9)	1.481 (10)
C(9)—C(10)	1.378 (9)	C(9)—C(14)	1.367 (9)
C(10)—C(11)	1.370 (9)	C(11)—C(12)	1.402 (8)
C(11)—C(15)	1.513 (10)	C(12)—C(13)	1.399 (9)
C(13)—C(14)	1.387 (9)		
C(12)—O(3)—C(16)	118.0 (7)	O(1)—N—O(2)	124.3 (7)
O(1)—N—C(1)	119.2 (7)	O(2)—N—C(1)	116.5 (8)
N—C(1)—C(2)	120.2 (7)	N—C(1)—C(6)	118.4 (7)
C(2)—C(1)—C(6)	121.5 (7)	C(3)—C(2)—C(1)	119.6 (7)
C(2)—C(3)—C(4)	121.0 (7)	C(3)—C(4)—C(5)	117.5 (6)
C(3)—C(4)—C(7)	123.1 (6)	C(5)—C(4)—C(7)	119.4 (6)
C(4)—C(5)—C(6)	121.1 (7)	C(1)—C(6)—C(5)	119.3 (7)
C(4)—C(7)—C(8)	126.5 (7)	C(7)—C(8)—C(9)	127.2 (7)
C(8)—C(9)—C(10)	118.7 (6)	C(8)—C(9)—C(14)	123.6 (7)
C(10)—C(9)—C(14)	117.7 (8)	C(9)—C(10)—C(11)	123.5 (7)
C(10)—C(11)—C(12)	118.0 (6)	C(10)—C(11)—C(15)	121.4 (7)
C(12)—C(11)—C(15)	120.5 (7)	O(3)—C(12)—C(11)	116.0 (6)
O(3)—C(12)—C(13)	124.2 (6)	C(11)—C(12)—C(13)	119.8 (6)
C(12)—C(13)—C(14)	119.1 (7)	C(9)—C(14)—C(13)	121.9 (7)
O(3)—C(12)—C(11)—C(10)	178.1 (10)		
O(3)—C(12)—C(13)—C(14)	-178.6 (11)		
O(2)—N—C(1)—C(6)	170.4 (11)		
O(1)—N—C(1)—C(6)	-7.8 (8)		
N—C(1)—C(6)—C(5)	-179.4 (12)		
C(3)—C(4)—C(7)—C(8)	1.5 (8)		
C(5)—C(4)—C(7)—C(8)	-179.8 (13)		
C(7)—C(8)—C(9)—C(10)	-175.9 (13)		
C(8)—C(9)—C(10)—C(11)	178.2 (12)		
C(13)—C(12)—C(11)—C(15)	179.2 (1)		
C(16)—O(3)—C(12)—C(11)	-178.7 (9)		
O(3)—C(12)—C(11)—C(15)	-1.0 (7)		
O(2)—N—C(1)—C(2)	-10.5 (8)		
O(1)—N—C(1)—C(2)	171.3 (12)		
N—C(1)—C(2)—C(3)	179.8 (12)		
C(2)—C(3)—C(4)—C(7)	-179.4 (11)		
C(4)—C(7)—C(8)—C(9)	-179.1 (15)		
C(6)—C(5)—C(4)—C(7)	179.7 (12)		
C(7)—C(8)—C(9)—C(14)	4.8 (9)		
C(8)—C(9)—C(14)—C(13)	-178.9 (12)		
C(15)—C(11)—C(10)—C(9)	-178.5 (13)		
C(16)—O(3)—C(12)—C(13)	1.0 (7)		

Space group and approximate cell dimensions of the crystal were determined using Weissenberg and precession photography (Suh, Suh, Ko, Aoki & Yamazaki, 1988). The systematic absences  $hkl$  for  $k+l = 2n$ ,  $Ok_l$  for  $k, l = 2n$ ,  $h0l$  for  $h, l = 2n$ ,  $hk0$  for  $k = 2n$ ,  $h00$  for  $h = 2n$  and  $0k0$  for  $k = 2n$  uniquely defined the non-centrosymmetric orthorhombic space group *Aba2*. Data were corrected for Lorentz and polarization effects. The structure was solved by the application of direct methods with *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and refined by full-matrix least squares using *SHELX76* (Sheldrick, 1976), with anisotropic displacement parameters for all the non-H atoms. All H atoms were located from difference Fourier maps. Geometric calculations were performed using *GEOM* (Shin, 1978). All computations were performed using the MicroVAX 3400 computer at Chungnam National University.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HL1045). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 6-Chloro-4(1H)-cinnolinone

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### Abstract

The title compound, C<sub>8</sub>H<sub>5</sub>ClN<sub>2</sub>O, crystallized with two molecules in the asymmetric unit. The geometries of the independent molecules are similar to within 2σ limits and closely resemble the geometries observed for unsubstituted and 1-alkyl-substituted