Crystal Structure of 3-Methyl-4-Methoxy-4′-Nitrostilbene

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Abstract

The crystal structure of the title compound was determined from single crystal X-ray diffraction study : $C_{16}H_{15}NO_3$, Mr=271.316, orthorhombic, Aba2, a=15.750(3), b=13.470(2), c=13.356(2) Å, V=2833 Å^3, Z=8, Dx=1.26 Mgm^{-3}, λ(MoK α) =0.71069 Å, μ=0.51mm^{-1}, F(000)=1136, T=291 K, R=0.0414 for 728 unique observed [$F \geq 3\sigma(F)$] reflections and 240 parameters. The molecule is nearly planar within 0.2 Å with the torsion angle -179(2)° for C(4)-C(7)-C(8)-C(9). The intermolecular interactions are mainly by van der Waals force with the nearest intermolecular distance 3.647 Å between O(3) and C(4) translated by half unit along b- and c- axes.

I. Introduction

The considerable potential of organic nonlinear optical materials for optical device application is now well established[1]. 3-methyl-4-methoxy-4'-nitrostilbene(MMONS) shows one of the largest powder second harmonic generation(SHG)signals(1250×Urea)[2]. MMONS is a typical organic material in which Van der Waals interactions and permanent dipole-dipole interactions are responsible for the intermolecular binding. As a consequence this results in relatively low melting points and high vapor pressure. In order to understand the basic nonlinear optical properties, thermal and mechanical properties, we carried out the X-ray structure analysis of MMONS crystal.

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Table 1. Atomic coordinates and temperature factors ($Å^2 \times 10^3$) with e. s. d.'s in paparentheses for $C_{16}H_{15}NO_3$

atom	x	y	z	Ueq*/Uiso
O(1)	0.2689(3)	0.2193(3)	0.2064(0)	64
O(2)	0.4588(4)	-0.1941(4)	-0.6357(6)	91
O(3)	0.5353(5)	-0.2812(5)	-0.5342(6)	106
N	0.4838(4)	-0.2151(6)	-0.5524(6)	69
C(1)	0.2928(4)	0.1712(5)	0.1223(6)	50
C(2)	0.3472(4)	0.0899(5)	0.1358(6)	53
C(3)	0.3711(5)	0.0370(6)	0.0529(7)	57
C(4)	0.3469(4)	0.0616(5)	-0.0431(7)	58
C(5)	0.2938(5)	0.1410(5)	-0.0549(7)	59
C(6)	0.2665(4)	0.1974(5)	0.0258(7)	56
C(7)	0.3787(5)	0.0006(6)	-0.1274(7)	60
C(8)	0.3664(5)	0.0159(6)	-0.2235(7)	56
C(9)	0.3973(4)	-0.0459(4)	-0.3058(7)	47
C(10)	0.4435(4)	-0.1324(4)	-0.2911(6)	51
C(11)	0.4717(4)	-0.1872(5)	-0.3703(8)	55
C(12)	0.4535(4)	-0.1569(5)	-0.4663(8)	55
C(13)	0.4064(5)	-0.0738(6)	-0.4844(7)	60
C(14)	0.3785(6)	-0.0185(6)	-0.4061(7)	63
C(15)	0.2126(6)	0.3005(7)	0.1968(9)	78
C(16)	0.3772(7)	0.0612(8)	0.2395(7)	73
H(3)	0.407(4)	-0.019(5)	-0.940(5)	73(25)
H(5)	0.269(4)	-0.159(4)	-0.116(4)	45(17)
H(6)	0.217(4)	0.250(5)	0.018(5)	77(23)
H(7)	0.416(4)	-0.058(4)	-0.112(4)	54(18)
H(8)	0.343(4)	0.081(5)	-0.243(4)	53(18)
H(10)	0.460(4)	-0.156(5)	-0.215(5)	73(22)
H(11)	0.498(3)	-0.249(4)	-0.368(4)	25(14)
H(13)	0.396(3)	-0.054(3)	-0.545(4)	20(14)
H(14)	0.338(5)	0.032(5)	-0.422(5)	85(29)
H(15A)	0.158(4)	0.284(5)	-0.842(6)	77(21)
H(15B)	0.233(3)	0.350(4)	-0.854(4)	40(15)
H(15C)	0.207(4)	0.321(4)	-0.741(5)	45(19)
H(16A)	0.330(5)	0.048(6)	0.278(6)	86(28)
H(16B)	0.402(6)	-0.018(8)	0.241(7)	143(37)
H(16C)	0.406(5)	0.111(5)	0.271(5)	75(24)

*$U_{eq} = \frac{1}{3}(U_{11}+U_{22}+U_{33})$

Table 2. Bond distance (Å) and angles (°) with e. s. d.'s in parentheses.

O(1)-C(1)	1.351(7)	O(1)-C(15)	1.413(9)	O(2)-N	1.213(8)
O(3)-N	1.228(7)	N-C(12)	1.471(9)	C(1)-C(2)	1.402(8)
C(1)-C(6)	1.399(9)	C(2)-C(3)	1.370(9)	C(2)-C(16)	1.513(10)
C(3)-C(4)	1.378(9)	C(4)-C(5)	1.367(9)	C(4)-C(7)	1.481(10)
C(5)-C(6)	1.387(9)	C(7)-C(8)	1.315(8)	C(8)-C(9)	1.463(9)
C(9)-C(10)	1.389(8)	C(9)-C(14)	1.420(10)	C(10)-C(11)	1.365(9)
C(11)-C(12)	1.376(10)	C(12)-C(13)	1.365(10)	C(13)-C(14)	1.357(10)
C(5)-H(5)	0.94(6)	C(6)-H(6)	1.05(6)	C(7)-H(7)	1.01(6)
C(8)-H(8)	0.99(6)	C(10)-H(10)	1.10(6)	C(11)-H(11)	0.93(5)
C(13)-H(13)	0.87(5)	C(14)-C(14)	0.95(7)	C(15)-C(15A)	1.03(7)
C(15)-H(15B)	1.01(5)	C(15)-C(15C)	0.88(6)	C(16)-H(16A)	0.92(8)
C(16)-H(16B)	1.13(10)	C(16)-H(16C)	0.91(7)		

C(1)-O(1)-C(15)	118.0(7)	O(2)-N-O(3)	124.3(7)
O(2)-N-C(12)	119.2(7)	O(3)-N-C(12)	116.5(8)
O(1)-C(1)-C(2)	116.0(6)	O(1)-C(1)-C(6)	124.2(6)
C(2)-C(1)-C(6)	119.8(6)	C(1)-C(2)-C(3)	118.0(6)
C(1)-C(2)-C(16)	120.5(7)	C(3)-C(2)-C(160	121.4(7)
C(2)-C(3)-C(4)	123.5(7)	C(3)-C(4)-C(5)	117.7(8)
C(3)-C(4)-C(7)	118.7(6)	C(5)-C(4)-C(7)	123.6(7)
C(4)-C(5)-C(6)	121.9(7)	C(1)-C(6)-C(5)	119.1(7)
C(4)-C(7)-C(8)	127.2(7)	C(7)-C(8)-C(9)	126.5(7)
C(8)-C(9)-C(10)	123.1(6)	C(8)-C(9)-C(14)	119.4(6)
C(10)-C(9)-C(14)	117.5(6)	C(9)-C(10)-C(11)	121.0(7)
C(10)-C(11)-C(12)	119.6(7)	N-C(12)-C(11)	120.2(7)
N-C(12)-C(13)	118.4(7)	C(11)-C(12)-C(13)	121.5(7)
C(12)-C(13)-C(14)	119.3(7)	C(9)-C(14)-C(13)	121.1(7)
C(2)-C(3)-H(3)	120(4)	C(4)-C(3)-H(3)	117(4)
C(4)-C(5)-H(5)	124(3)	C(6)-C(5)-H(5)	114(3)
C(1)-C(6)-H(6)	118(4)	C(5)-C(6)-H(6)	121(4)
C(4)-C(7)-H(7)	119(3)	C(8)-C(7)-H(7)	114(3)
C(7)-C(8)-H(8)	117(3)	C(9)-C(8)-H(8)	116(3)
C(9)-C(10)-H(10)	120(3)	C(11)-C(10)-H(10)	119(3)
C(10)-C(11)-H(11)	127(4)	C(12)-C(11)-H(11)	113(3)
C(12)-C(13)-H(13)	122(3)	C(14)-C(13)-H(13)	119(3)
C(9)-C(14)-H(13)	121(7)	C(9)-C(14)-H(14)	122(5)
C(13)-C(14)-H(14)	116(5)	O(1)-C(15)-H(15A)	114(4)
O(1)-C(15)-H(15B)	94(5)	H(15A)-C(15)-H(15C)	103(4)
H(15A)-C(15)-H(15B)	94(5)	H(15A)-C(15)-H(15C)	117(6)
H(15B)-C(15)-H(15C)	117(5)	C(2)-C(16)-H(16A)	108(5)
C(2)-C(16)-H(16B)	111(5)	C(2)-C(16)-H(16C)	113(4)
H(16A)-C(16)-H(16B)	95(7)	H(16A)-C(16)-H(16C)	107(7)
H(16B)-C(16)-H(16C)	120(7)		

Ⅱ. Experiment

MMONS was synthesized by the Witting reaction of diethyl-p-nitrobenzylphosphonate and 3-methyl-p-anisaldehyde. The product was checked and confirmed by ^1H NMR and high resolution mass spectrum. The material was purified by recrystallization in methylethyl-ketone(MEK) solution and further purification was made using liquid column chromatography method. The sample crystal used in this study was prepared by slow evaporation of MEK at room temperature.

Space group and approximate cell dimensions of the crystal were determined by preliminary

Table 3. Selected torsion angles(°) with e.s.d.'s in parentheses.

O(1)-C(1)-C(2)-C(3)	178.1(10)	O(1)-C(1)-C(2)-C(16)	-1.0(7)
O(1)-C(1)-C(6)-C(5)	-178.6(11)	O(2)-N-C(12)-C(11)	171.3(12)
O(2)-N-C(12)-C(13)	-7.8(8)	O(3)-N-C(12)-C(11)	-10.5(8)
O(3)-N-C(12)-C(13)	170.4(11)	N-C(12)-C(13)-C(14)	-179.4(12)
C(2)-C(3)-C(4)-C(7)	178.2(12)	C(3)-C(4)-C(7)-C(8)	-175.9(13)
C(4)-C(7)-C(8)-C(9)	-179.1(15)	C(5)-C(4)-C(7)-C(8)	4.8(9)
C(6)-C(1)-C(2)-C(16)	179.2(11)	C(7)-C(4)-C(5)-C(6)	-178.9(12)
C(7)-C(8)-C(9)-C(10)	1.5(8)	C(7)-C(8)-C(9)-C(14)	-179.8(13)
C(8)-C(9)-C(10)-C(11)	-179.4(11)	C(8)-C(9)-C(14)-C(13)	179.7(12)
C(10-C(11)-C(12)-N	179.8(12)	C(15)-O(1)-C(1)-C(2)	-178.7(9)
C(16)-C(2)-C(3)-C(4)	-178.5(13)	C(15)-O(1)-C(1)-C(6)	1.0(7)

experiment using Weissenberg and precession photography[3]. The systematic absences $h k \ell$ for $k+\ell=2n$, $0k\ell$ for k, $\ell=2n$, $h0\ell$ for h, $\ell=2n$, $hk0$ for $k=2n$, $h00$ for $h=2n$ and $0k0$ for $k=2n$ uniquely defined the non-centrosymmetric orthorhombic space group Aba2[4].

A yellow crystal of dimensions of 0.33×0.46×0.30mm was mounted in glass fiber and was secured to the goniometer head on Enraf-Nonius CAD-4 diffractometer, generator settings 40kV 20mA, controlled by a Micro PDP11/53 computer. The accurate cell parameters were refined from setting angles of 25 reflections in the range $10.09° < \theta < 14.13°$, and intensity data for 1221 independent reflections with $0 \le h \le 18$, $0 \le k \le 15$, $0 \le \ell \le 15$ were collected using graphite-monochromated MoKα radiation and $\omega/2\theta$ scan mode, ω-scan width = $(0.8+0.34\tan\theta)°$, $[(\sin\theta)/\lambda]_{max}=0.5723\,Å^{-1}$. Three standard reflections (751), (60$\bar{6}$) and (740) measured every 6000 seconds showed no singnificant intensity variation over the total exposure time. Lorentz and polarization corrections were applied to the intensity data but no correction for absorption was considered.

The structure was solved by the application of direct methods with MULTAN87[5] and refined by full-matrix least-squares on F (SHELX76[6]) with anisotropic thermal factors for all the non-H atoms and isotropic thermal factors for H atoms located from difference Fourier maps. Function minimized was $\Sigma\omega(|F_o|-(|F_o|))^2$, where $\omega=[\sigma^2(F_o)+0.000824F_o^2]^{-1}$. Number of parameters refined was 240.

Final reliability factors for 728 unique observed [$F \ge 3\sigma(F)$] reflections were R=0.0414, ωR=0.0415 and S=1.068 with average $\triangle/\sigma$=0.008 in last cycle and $\triangle\rho_{max}/\triangle\rho_{min}$=0.1306/-0.1645 e Å^{-3} in final $\triangle$F map. The final positional and equivalent isotropic thermal parameters for non-H atoms and isotropic thermal parameters for H-atoms are given in Table 1*. Geometric calculations on the molecular structure were done using GEOM program[7]. All computations were performed using the Micro VAX/VMS 3400 computer at Chungnam National University.

Ⅲ. Discussion

The bond lengths, angles and torsion angles are

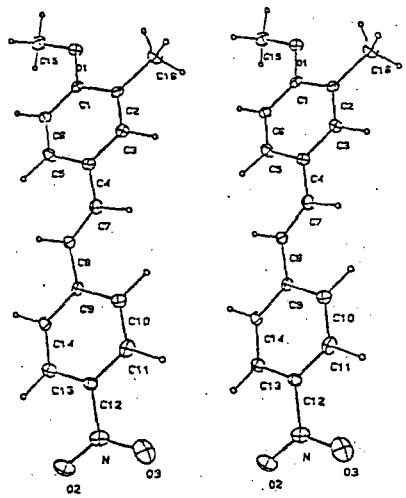

Fig. 1. Stereoscopic view of the title compound with an atom-numbering scheme.

*The list of observed and calculated structure factors based on the parameters in Table 1, may be obtained from authors

listed in Tables 2 and 3 respectively. Figure 1 shows a stereoscopic view of one molecule with the atom-numbering scheme drawn with ORTEP.[8]

As shown in Table 2, the twelve C-C bond lengths in the aromatic phenyl rings range from 1.357(10) Å to 1.420(10) Å with mean value 1.381 (9) Å which is comparable with the normal C-C resonance bond distance of 1.395 Å [9], and valence angles from 117.5(6)° to 123.5(7)° with mean value 120.0(7)° . C(1)-O(1) bond length 1.351(7) Å, O(1) -C(15) bond length 1.413(9) Å and C(2)-C(16) bond length 1.513(10) Å are in good agreement with the respective bond length 1.366 (4) Å, 1.427(7) Å and 1.505(5) Å in 9-Methoxy-1 1-demethylellipticine[10]. The mean N-O bond length 1.22 Å of nitro group shows that their bond order is 1.5.

The C(7)-C(8) bond length 1.315(8) Å and the average bond distance 1.472 Å of C(4)-C(7) and C(8)-C(9) connecting two benzene rings show double and single bond character, respectively. To diminish repulsions between C(5) and C(8) and between C(7) and C(10), the angles 123.6 (7)° of C(5)-C(4)-C(7) and 123.1(6)° of C(8) -C(9)-C(10) are larger than 118.7(6)° of C(3) -C(4)-C(7) and 119.4(6)° of C(8)-C(9)-C(14). The dihedral angle between the two phenyl rings is 15.8(9)° and the torsion angle of C(4)-C(7) -C(8)-C(9) is -179(2)° as shown in Table 4, so that the stilbene molecule in MMONS is planar within 0.14 Å, and O(2), O(3), C(15) and C(16) atoms are deviated -0.06, 0.17, -0.09 and 0.15 Å respectively from the best plane. The similar planar arrangement had been found in the trans-stilbene[11]. The nitrobenzene group in MMONS is also planar within 0.2 Å with dihedral angle 18 (2)° between nitrophenyl ring and nitro group, whose conformation is comparable with those of nitrobenzene studied at -30℃ [12] and meta-nitroaniline[13] showing completely planar forms. These results make MMONS molecule have an approximately planar form within 0.2 Å.

The packing of the molecules in the unit cell viewed down c-axis is shown in Fig. 2 and the nearest intermolecular distance 3.647 Å between O(3) and C(4) [x, y-0.5, z-0.5] shows that the molecules are held together by van der Waals force.

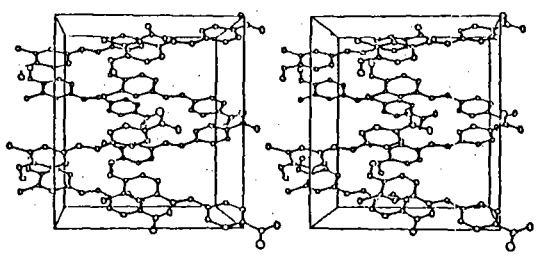

Fig. 2. A stereoview of a unit-cell packing for the molecule: orgin, lower left; b-axis, hoizontal; a-axis, vertical.

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