

O(4)—C(4)—C(4a)	123.4 (2)	C(5a)—C(9a)—N(10)	120.9 (2)
C(4)—C(4a)—C(10a)	120.1 (2)	C(9a)—N(10)—C(10a)	116.7 (2)
C(4)—C(4a)—N(5)	118.3 (2)	C(4a)—C(10a)—N(10)	122.7 (2)
N(5)—C(4a)—C(10a)	121.6 (2)	N(1)—C(10a)—N(10)	118.5 (2)
C(4a)—N(5)—C(5a)	117.3 (2)	N(1)—C(10a)—C(4a)	118.7 (2)
C(11)—N(1)—C(2)—N(3)	176.8 (2)		
C(11)—N(1)—C(10a)—C(4a)	-176.4 (2)		
C(11)—N(1)—C(2)—O(2)	-3.1 (4)		
C(11)—N(1)—C(10a)—N(10)	3.7 (3)		
N(1)—C(2)—N(3)—C(31)	-178.6 (2)		
C(31)—N(3)—C(4)—C(4a)	179.9 (2)		
C(31)—N(3)—C(4)—O(4)	-0.2 (4)		
O(2)—C(2)—N(3)—C(31)	1.3 (4)		
C(91)—C(9)—C(9a)—C(5a)	178.5 (2)		
C(7)—C(8)—C(9)—C(91)	-177.2 (2)		
C(91)—C(9)—C(9a)—N(10)	-0.9 (3)		

Table 3. Deviations from 120° of selected endocyclic bond angles in 1,3,9-MAll, 9-MAll and 1,3,8,9-MAll

Benzene ring	C(5a)	C(6)	C(7)	C(8)	C(9)	C(9a)
1,3,9-MAll	+0.2 (2)	-1.0 (2)	+0.7 (2)	+2.4 (2)	-2.4 (2)	-0.0 (2)
9-MAll	+0.6 (2)	-1.4 (2)	+0.8 (2)	+3.0 (2)	-2.5 (2)	-0.5 (2)
1,3,8,9-MAll	+0.0 (4)	-1.9 (5)	+3.4 (5)	+0.2 (5)	-2.9 (4)	+1.1 (4)
Pyrimidine ring	N(1)	C(2)	N(3)	C(4)	C(4a)	C(10a)
1,3,9-MAll	+3.0 (2)	-2.7 (2)	+5.8 (2)	-5.1 (2)	+0.1 (2)	-1.3 (2)
9-MAll	+4.3 (2)	-4.3 (2)	+6.9 (2)	-5.2 (2)	-0.3 (2)	-1.5 (2)
1,3,8,9-MAll	+1.6 (4)	-1.2 (4)	+4.7 (4)	-4.7 (4)	+0.1 (4)	-0.6 (4)

Corrections for background, decay, Lorentz and polarization factors, but not for absorption effects, were included in the data reduction. The structure was solved by direct methods with the program *MITHRIL* (Gilmore, 1983), which resulted in reliable positions for all 19 non-H atoms. The initial model was refined with *SHELX76* (Sheldrick, 1976). Four low- $\theta$  reflections had  $F_{\text{obs}}$  systematically lower than  $F_{\text{calc}}$  indicating extinction and were excluded from the last refinement.

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Lists of structure factors, anisotropic thermal parameters, least-squares-planes data and H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71382 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1075]

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## 3-(4-*tert*-Butylphenyl)-3-hydroxy-1-(4-methoxyphenyl)-2-propen-1-one: an SHG Active $\beta$ -Diketone

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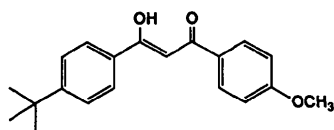
## Abstract

The molecular structure of 3-(4-*tert*-butylphenyl)-1-(4-methoxyphenyl)-1,3-propanedione in its crystal state was determined as an enol structure, 3-(4-*tert*-butylphenyl)-3-hydroxy-1-(4-methoxyphenyl)-2-propen-1-one (BPMP),  $C_{20}H_{22}O_3$ , with a disordered *tert*-butyl group attached to the benzene ring. BPMP has a powder second-order harmonic generation (SHG) efficiency ten times that of urea.

## Comment

Organic materials are popular in second-order harmonic generation (SHG) devices such as laser diodes because they show large optical non-linearities and offer architectural flexibility (Chemla & Zyss, 1987) compared with inorganic materials. However, the majority of organic compounds have centrosymmetric crystal structures and are therefore SHG inactive. There are also other associated problems, such as thermal instabilities, growth of a large single crystal and processing for SHG devices. In addition, organic materials with large hyperpolarizabilities absorb light in longer-wavelength regions. In an attempt to develop new organic SHG materials, we

found that the title compound has great SHG activity. Crystals of BPMP, grown from acetonitrile, chloroform, ethyl acetate, *n*-hexane, methanol and toluene solutions, showed significant SHG activities. The SH intensity was measured using the conventional powder technique (Kurtz & Perry, 1968). The transmission cut-off wavelength for this compound was shorter than 410 nm in acetonitrile solution. The cut-off wavelength for BPMP depends on the keto-enol tautomerism and the solvents used for the measurement. To calculate and measure the linear and non-linear optical properties of BPMP crystals and to design and fabricate the SHG devices, the structure of BPMP was determined by X-ray crystallography.



Keto-enol tautomerism is a well known feature in  $\beta$ -diketone derivatives and their molecular and crystal structures have been investigated (Engebretson & Rundle, 1964; Semmingsen, 1977). The C(8)—C(9) bond length [1.365 (8) Å] is shorter than that of C(7)—C(8) [1.407 (8) Å], and O(2)—C(7) [1.264 (6) Å] is shorter than O(3)—C(9) [1.318 (6) Å]. Typical bond distances of C=C, C—C, C=O and C—O are 1.34, 1.54, 1.23 and 1.43 Å, respectively. The O(3)—C(9)—C(8) bond angle is approximately 120°. From the C(7)—C(8)—C(9)—C(10) and O(3)—C(9)—C(8)—C(7) dihedral angles, the four C atoms and O(3) are inferred to be almost on the same plane. These data support the fact that C(8) and C(9) are attached *via* C=C rather than C—C. H(23) and H(8) were located on a difference Fourier map. The bond distance between O(3) and H(23) is 1.240 Å and between O(2) and H(23), 1.358 Å. From these geometric parameters, it is suggested that the  $\beta$ -diketone skeleton that links the two benzene rings in BPMP is an enol structure and the intramolecular hydrogen bond between the H atom of the hydroxy group, O(3)—H(23), and O(2) plays an important role. The *tert*-butyl group of BPMP was disordered and hence, two types of *tert*-butyl groups were observed and the ratio of their site occupancies was 1:1. They are represented as C(17), C(18), C(19), C(20) and C(17), C(21), C(22), C(23) in Fig. 1.

BPMP was refined as an enol structure, similar to chalcon derivatives, which are known to have large non-linear optical properties (Goto *et al.*, 1990; Ogawa, Yoshimura, Kaji, Kagawa & Kakuta, 1992). The crystal structure is shown in Fig. 2. BPMP molecules are arranged in the same direction along the crystallographic *c* axis; the large non-linear optical susceptibility of BPMP crystals arises from such a molecular packing.

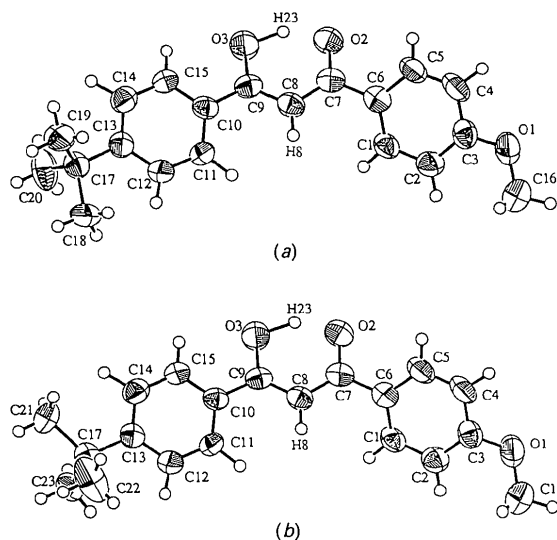


Fig. 1. Perspective view of the molecule (ORTEPII; Johnson, 1976). Two types of disordered *tert*-butyl groups are represented: (a) C(17)—C(18)—C(19)—C(20) and (b) C(17)—C(21)—C(22)—C(23).

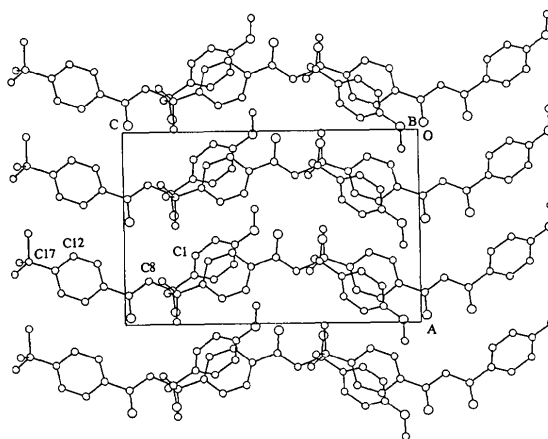


Fig. 2. Packing diagram viewed down the *b* axis.

## Experimental

### Crystal data

C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>

*M<sub>r</sub>* = 310.39

Orthorhombic

*Pna*2<sub>1</sub>

*a* = 10.6819 (9) Å

*b* = 9.964 (1) Å

*c* = 16.2694 (9) Å

*V* = 1731.6 (4) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.191 Mg m<sup>-3</sup>

Cu *K*α radiation

λ = 1.54178 Å

Cell parameters from 25

reflections

θ = 37.4–39.7°

μ = 0.595 mm<sup>-1</sup>

*T* = 296 K

Plate

0.40 × 0.40 × 0.15 mm

Colourless

**Data collection**

Rigaku AFC-5R diffractometer  
 $\omega$ -2 $\theta$  scans  
 Absorption correction: empirical (DIFABS; Walker & Stuart, 1983)  
 $T_{\min} = 0.78$ ,  $T_{\max} = 1.47$   
 1517 measured reflections  
 1517 independent reflections

1047 observed reflections  
 $[I > 3.00\sigma(I)]$   
 $\theta_{\max} = 60^\circ$   
 $h = -11 \rightarrow 0$   
 $k = -11 \rightarrow 0$   
 $l = -11 \rightarrow 0$   
 3 standard reflections monitored every 150 reflections  
 intensity variation: none

**Refinement**

Refinement on  $F$   
 $R = 0.048$   
 $wR = 0.064$   
 $S = 1.59$   
 1047 reflections  
 H-atom parameters not refined  
 $w = 1/\sigma^2(F_o)$   
 $(\Delta/\sigma)_{\max} = 0.07$

$\Delta\rho_{\max} = 0.16 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: secondary  
 Extinction coefficient:  $0.1207 \times 10^{-5}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

O(2)—C(7)—C(6)—C(1)	-152.9 (5)
O(2)—C(7)—C(6)—C(5)	30.4 (8)
O(2)—C(7)—C(8)—C(9)	-0.9 (8)
O(3)—C(9)—C(8)—C(7)	2.4 (8)
O(3)—C(9)—C(10)—C(11)	172.2 (5)
O(3)—C(9)—C(10)—C(15)	-10.4 (7)
C(1)—C(6)—C(7)—C(8)	29.7 (8)
C(5)—C(6)—C(7)—C(8)	-146.9 (5)
C(6)—C(7)—C(8)—C(9)	176.4 (5)
C(7)—C(8)—C(9)—C(10)	-173.3 (5)
C(8)—C(9)—C(10)—C(11)	-11.9 (8)
C(8)—C(9)—C(10)—C(15)	165.5 (5)

BPMP was purchased from Ogawa & Co. Ltd. To evaluate the crystal structure, single crystals were grown by slow evaporation of an acetonitrile solution at room temperature.

The SHG powder measurements were performed following the standard Kurtz & Perry (1968) technique. A 1064 nm Q-switched Nd<sup>3+</sup>:YAG laser (10 Hz, 8 ns pulse duration) was used. The SH intensity was compared with that of the standard nonlinear compound, urea.

All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). *PLUTO* (Motherwell & Clegg, 1978) was used for the molecular graphics.

The authors thank Dr M. Shiro (Rigaku Corporation) for performing the X-ray measurements, analysis of the crystal structure and helpful discussions. They are grateful to OGAWA & Co. Ltd for providing the BPMP.

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

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$
O(1)	0.5144 (5)	0.1096 (5)	-0.4411	6.8 (2)
O(2)	0.9337 (4)	0.0743 (5)	-0.1702 (4)	6.1 (2)
O(3)	0.9631 (3)	0.0830 (5)	-0.0195 (4)	6.8 (2)
C(1)	0.6394 (5)	0.1984 (5)	-0.2391 (4)	4.7 (3)
C(2)	0.5636 (5)	0.2046 (6)	-0.3084 (4)	5.3 (3)
C(3)	0.5870 (5)	0.1174 (6)	-0.3732 (4)	5.1 (3)
C(4)	0.6893 (6)	0.0332 (7)	-0.3697 (4)	6.0 (3)
C(5)	0.7674 (6)	0.0327 (6)	-0.3018 (4)	5.6 (3)
C(6)	0.7422 (5)	0.1153 (5)	-0.2349 (4)	4.5 (2)
C(7)	0.8204 (5)	0.1072 (5)	-0.1605 (5)	4.6 (2)
C(8)	0.7717 (5)	0.1293 (6)	-0.0813 (4)	4.6 (2)
C(9)	0.8437 (5)	0.1143 (5)	-0.0126 (4)	4.5 (2)
C(10)	0.7974 (5)	0.1214 (5)	0.0721 (4)	4.2 (2)
C(11)	0.6782 (5)	0.1683 (6)	0.0921 (4)	4.9 (3)
C(12)	0.6357 (5)	0.1673 (6)	0.1725 (4)	5.1 (3)
C(13)	0.7102 (5)	0.1192 (5)	0.2362 (4)	4.4 (3)
C(14)	0.8282 (5)	0.0727 (6)	0.2170 (5)	5.2 (3)
C(15)	0.8712 (5)	0.0756 (6)	0.1358 (5)	4.8 (3)
C(16)	0.4020 (7)	0.1817 (8)	-0.4440 (5)	7.5 (4)
C(17)	0.6620 (5)	0.1176 (6)	0.3244 (4)	4.9 (3)
C(18)	0.514 (1)	0.154 (2)	0.326 (1)	7.7 (8)
C(19)	0.665 (2)	-0.026 (1)	0.356 (1)	7.2 (8)
C(20)	0.728 (2)	0.217 (2)	0.373 (1)	8.0 (1)
C(21)	0.771 (1)	0.060 (2)	0.3890 (8)	7.1 (8)
C(22)	0.548 (2)	0.041 (2)	0.331 (1)	10 (1)
C(23)	0.647 (1)	0.268 (2)	0.355 (1)	6.5 (7)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O(2)—C(7)	1.264 (6)	C(7)—C(8)	1.407 (8)
O(3)—C(9)	1.318 (6)	C(8)—C(9)	1.365 (8)
O(3)—H(23)	1.240	C(9)—C(10)	1.466 (7)
C(6)—C(7)	1.474 (8)	O(2)···H(23)	1.358
O(2)—C(7)—C(6)	117.1 (5)	O(3)—C(9)—C(8)	120.1 (5)
O(2)—C(7)—C(8)	120.6 (5)	O(3)—C(9)—C(10)	114.6 (5)
C(6)—C(7)—C(8)	122.3 (4)	C(8)—C(9)—C(10)	125.1 (4)
C(7)—C(8)—C(9)	121.6 (4)		

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71398 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1029]

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