in the title compound. In both these structures there are said to be weak bonding interactions between phosphorus and the O atoms of the *ortho*-methoxy groups with contact distances varying between 2.819 and 2.996 Å. These contacts are attributed to an interaction between the lone pair at the O atom and a dipolar resonance form of the P=Se double bond. Such an interaction was also invoked in the description of the structure of $[Ph_2P(CH_2Ph)(C_6H_4OMe)]Br$, in which the P—O distance is 2.88 Å (Wood, Wilkholm & McEwan, 1977). It might reasonably be expected that such effects would be at least as pronounced in the title compound. In each of the crystallographically distinct molecules there are three shorter [P1—O4 = 2.869 (3), P1—O5 = 2.841 (3) and P1—O8 = 2.823 (4); P1*a*—O4*a* = 2.858 (3), P1*a*—O5*a* = 2.836 (4) and P1*a*—O8*a* = 2.784 (4) Å] and three longer [P1—O2 = 3.066 (3), P1—O7 = 3.124 (4) and P1—O10 = 3.168 (3); P1*a*—O2*a* = 3.082 (4), P1*a*—O7*a* = 3.075 (3) and P1*a*—O10*a* = 3.179 (4) Å] P···O contacts. The shorter set of distances are comparable with the previous data in which some dipolar interaction is invoked.

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Thiophene Chalcone

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Abstract. 3-(4-Methylphenyl)-1-(3-thienyl)-2-propen-1-one, $C_{14}H_{12}OS$, $M_r = 228.31$, orthorhombic, *Fdd*2, $a = 18.787$ (7), $b = 43.46$ (2), $c = 5.828$ (2) Å, $V = 4758$ (3) Å^3, $Z = 16$, $D_x = 1.27$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073, $\mu = 2.35$ cm^{-1}, $F(000) = 1920$, $T = 296$ K, final $R = 0.041$ for 767 observed reflections with $I > 3\sigma(I)$. The torsion angle is 4° for O—C(3)—C(2)—C(1) of the central C_2H_2CO group. The dihedral angle between the phenyl ring and thiophene is 7.85°.

Introduction. The chalcone derivatives are newly developed organic crystals with nonlinear optical coefficients (Fichou, Watanabe, Takeda, Miyata, Goto & Nakayama, 1988). In order to explore the relationship between their structure and nonlinear optical properties, we synthesized a series of substituted chalcones. The title compound is one of them. The second harmonic generation (SHG) efficiencies of the compound were measured by Kurtz & Perry (1968) powder technique; the intensity is three times larger than that of KDP ($d_{36} = 0.63$ pm V^{-1}) standard. The effect is not particularly strong. The crystal structure is determined and discussed.

Experimental. The title compound was prepared by acyloin condensation of *p*-methylbenzaldehyde with 3-acetylthiophene at room temperature (Migrdichian, 1957). The crystals were obtained from ethanol solution by evaporation. A colourless transparent prismatic crystal with approximate dimen-

0108-2701/93/061075-03$06.00

Table 1. *Atomic coordinates and equivalent isotropic temperature factors* (Å^2)

$B_{eq} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
S(1)	0.1362 (1)	0.13372 (4)	0.4469	7.0 (1)
O(1)	0.3110 (3)	0.1900 (1)	0.900 (1)	6.7 (3)
C(1)	0.3609 (3)	0.2305 (1)	0.559 (1)	4.3 (3)
C(2)	0.3093 (3)	0.2104 (1)	0.524 (1)	4.7 (3)
C(3)	0.2862 (3)	0.1891 (1)	0.707 (2)	4.6 (3)
C(11)	0.1950 (3)	0.1635 (1)	0.449 (1)	5.2 (3)
C(12)	0.2318 (3)	0.1655 (1)	0.650 (1)	4.2 (3)
C(13)	0.2111 (3)	0.1417 (1)	0.806 (1)	5.5 (3)
C(14)	0.1606 (3)	0.1223 (1)	0.721 (1)	5.0 (3)
C(21)	0.3895 (3)	0.2536 (1)	0.402 (1)	3.9 (3)
C(22)	0.3598 (3)	0.2596 (1)	0.188 (1)	4.3 (3)
C(23)	0.3878 (3)	0.2824 (1)	0.050 (1)	4.8 (3)
C(24)	0.4468 (3)	0.2996 (1)	0.116 (1)	4.3 (3)
C(25)	0.4764 (3)	0.2932 (1)	0.329 (1)	4.5 (3)
C(26)	0.4489 (3)	0.2708 (1)	0.469 (1)	4.3 (3)
C(27)	0.4782 (3)	0.3243 (1)	−0.036 (2)	6.2 (3)

Table 2. *Bond distances* (Å) *and angles* (°)

S(1)—C(11)	1.700 (6)	C(13)—C(14)	1.361 (9)
S(1)—C(14)	1.733 (8)	C(21)—C(22)	1.395 (8)
O(1)—C(3)	1.216 (8)	C(21)—C(26)	1.400 (7)
C(1)—C(2)	1.321 (7)	C(22)—C(23)	1.379 (8)
C(1)—C(21)	1.461 (8)	C(23)—C(24)	1.388 (8)
C(2)—C(3)	1.478 (9)	C(24)—C(25)	1.388 (9)
C(3)—C(12)	1.487 (8)	C(24)—C(27)	1.514 (9)
C(11)—C(12)	1.36 (1)	C(25)—C(26)	1.375 (9)
C(12)—C(13)	1.432 (8)		

C(11)—S(1)—C(14)	92.2 (3)	C(13)—C(14)—S(1)	110.0 (5)
C(2)—C(1)—C(21)	128.9 (6)	C(22)—C(21)—C(26)	118.0 (5)
C(1)—C(2)—C(3)	121.2 (6)	C(22)—C(21)—C(1)	123.0 (5)
O(1)—C(3)—C(2)	122.2 (6)	C(26)—C(21)—C(1)	119.0 (6)
O(1)—C(3)—C(12)	119.7 (6)	C(23)—C(22)—C(21)	120.3 (5)
C(2)—C(3)—C(12)	118.1 (6)	C(22)—C(23)—C(24)	121.9 (6)
C(12)—C(11)—S(1)	112.7 (5)	C(25)—C(24)—C(23)	117.4 (6)
C(11)—C(12)—C(13)	111.2 (5)	C(25)—C(24)—C(27)	120.5 (6)
C(11)—C(12)—C(3)	126.0 (6)	C(23)—C(24)—C(27)	122.0 (6)
C(13)—C(12)—C(3)	122.8 (6)	C(26)—C(25)—C(24)	121.5 (5)
C(14)—C(13)—C(12)	113.8 (6)	C(25)—C(26)—C(21)	120.8 (6)

sions 0.6 × 0.25 × 0.15 mm was mounted on a glass fibre in a random orientation. Preliminary examination and intensity-data collection were performed on a Rigaku MSC/AFC-5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters were determined by least squares from 20 reflections with $12 < 2\theta < 16°$. 1499 unique reflections were collected in the range $1 < 2\theta < 54°$ ($0 < h < 24$, $0 < k < 56$, $0 < l < 7$) by ω–2θ scans of ω-scan width $(1.10 + 0.35\tan\theta)°$ and scan speed 16° min^{-1}. 767 observed reflections with $I > 3\sigma(I)$ were used for structure determination. Three standard reflections ($\bar{4}80$, $2,\bar{1}\bar{2},0$, $\bar{3}91$) were monitored every 250 measurements and showed 0.3% variation in average intensity. Lorentz and polarization corrections were applied. The linear absorption coefficient was 2.35 cm^{-1} for Mo $K\alpha$ radiation. *DIFABS* (Walker & Stuart, 1983) empirical absorption corrections were applied, yielding relative transmission coefficients ranging from 0.9787 to 1.0000.

Table 3. *Selected least-squares planes*

Plane 1

Atoms defining plane	Distance (Å)	E.s.d.
C(11)	0.0071	0.0079
C(12)	0.0003	0.0068
C(13)	−0.0062	0.0077
C(14)	0.0113	0.0081
S(1)	−0.0001	0.0006
Additional atoms		
C(3)	−0.0148	

Mean deviation from plane = 0.0050 Å; $\chi^2 = 7.9$

Plane 2

Atoms defining plane	Distance (Å)	E.s.d.
C(21)	−0.0035	0.0065
C(22)	0.0083	0.0072
C(23)	−0.0065	0.0071
C(24)	0.0006	0.0070
C(25)	−0.0001	0.0079
C(26)	0.0021	0.0073
C(27)	0.0013	0.0090
Additional atoms		
C(1)	−0.0346	

Mean deviation from plane = 0.0032 Å; $\chi^2 = 5.4$

Plane 3

Atoms defining plane	Distance (Å)	E.s.d.
C(1)	0.0088	0.0071
C(2)	0.0052	0.0071
C(3)	−0.0100	0.0086
C(21)	−0.0065	0.0065
Additional atoms		
O(1)	−0.0828	
C(12)	0.0948	

Mean deviation from plane = 0.0076 Å; $\chi^2 = 4.4$

Plane 4

Atoms defining plane	Distance (Å)	E.s.d.
C(3)	0.0182	0.0086
C(2)	−0.0127	0.0071
C(1)	0.0047	0.0071
O(1)	−0.0025	0.0057
Additional atoms		
C(12)	0.1041	
C(21)	−0.0497	

Mean deviation from plane = 0.0095 Å; $\chi^2 = 10.2$

Dihedral angles between least-squares planes

Plane	Plane	Angle (°)	Plane	Plane	Angle (°)
2	1	7.85	4	1	7.52
3	1	5.75	4	2	9.33
3	2	6.94	4	3	2.52

All calculations were performed on a VAX computer with programs from the *TEXRAY* crystallographic software package (Molecular Structure Corporation, 1985). The structure was solved by direct methods. The position of the S atom was revealed from an *E* map and the *DIRDIF* (Beurskens, 1984) program was then applied. The structure was refined by full-matrix least-squares method with anisotropic thermal parameters for all non-H atoms, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ using weights $w = 1/\sigma^2(F_o)$. The coordinates of H atoms were added according to theoretical models and were included in the structure-factor calculations. The final cycle of refinement included 144 variable parameters for 767 reflections with $I > 3\sigma(I)$. The final values of the discrepancy factors were $R = 0.041$, $wR = 0.056$, $S = 1.43$, $(\Delta/\sigma)_{\max} = 0.01$. The maximum residual electron density was 0.15 e Å^{-3}. Scattering factors and f', f'' were taken from Cromer & Waber (1974).

Discussion. The final atomic coordinates and thermal parameters are given in Table 1. The bond lengths and angles are listed in Table 2. Several least-squares planes are given in Table 3. The molecular configuration and the packing of the molecules in the unit cell are shown in Figs. 1 and 2, respectively.* In general, bond lengths in conjugated systems are longer than double bonds and shorter than single bonds. Indeed, for the compound, C(1)—C(21), C(2)—C(3), C(3)—C(12), C(2)—C(1) and O(1)—C(3) bonds are 1.461 (8), 1.478 (9), 1.487 (8), 1.321 (7) and 1.216 (8) Å, respectively. These bonds are similar to the equivalent bonds found in 4-bromochalcone (Li, Pan & Su, 1992), 4′-methoxychalcone (Li, Huang & Su, 1992) and 4-bromo-4′-ethoxychalcone (Li, Huang, Su & Wang, 1992). The benzene ring, the thiophene ring and the O(1)—C(3)—C(2)—C(1) group are each closely planar, and the dihedral angles between the three planes are 7.85, 7.52 and 9.33°, respectively (Table 3). This shows the molecule to be more planar than the above three compounds. Because the torsion angle O(1)—C(3)—C(2)—C(1) of the central C_2H_2CO group is only 4°, it is suggested that an extended π-electron conjugated system is induced in the molecule and intramolecular charge transfer over the whole molecule is expected. According to the 'molecular engineering' theory (Nicoud & Twieg, 1987), the molecular net orientations are very important in an organic crystal for an efficient SHG. The unit cell contains 16 molecules which are stacked in four sheets. From Fig. 2 we see that molecules have opposite orientations within each sheet so that their molecular susceptibilities tend to cancel. The packing arrangement, which is not optimal for inducing nonlinear optical properties (Zyss & Chemla, 1987), is thus consistent with the observed SHG efficiency which is not particularly strong.

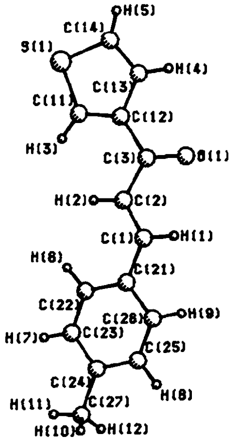

Fig. 1. The molecular structure of the title compound.

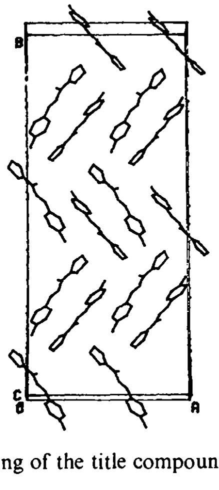

Fig. 2. The packing of the title compound in the unit cell.

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55856 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1026]