

$R = 5.73$ ,  $wR = 5.01\%$  and  $GOF = 0.81$  for all 3527 reflections [ $R = 3.08$ ,  $wR = 3.82\%$  for those 2291 data for which  $F_o > 6.0\sigma(F)$ ]. The function minimized during least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/[\sigma^2(F) + 0.0012F^2]$ . A final difference Fourier map showed no unusual features, having a residual electron density in the range  $-0.59$  to  $+0.97 \text{ e } \text{Å}^{-3}$  close to the position of the Ir atom and no other features above  $0.50 \text{ e } \text{Å}^{-3}$ . The absolute configuration was determined by  $\eta$  refinement [ $\eta = +1.07$  (6) for the initially chosen coordinates]. Final atom coordinates appear in Table 1.\* The molecular structure and atomic labeling scheme are shown in Fig. 1; this is an *ORTEP* plot (Johnson, 1976). Selected bond lengths and bond angles are collected in Table 2. The structure is ordered and there are no abnormally short intermolecular distances.

**Related literature.** In the following discussion corresponding values of bond lengths and angles from the related structural determination of disordered *trans*-[CH<sub>3</sub>(CO)Ir(PPh<sub>3</sub>)<sub>2</sub>] (Rees, Churchill, Li & Atwood, 1985) are listed in curly brackets for ease of comparison. It should be noted that in the earlier determination the Ir—CO and Ir—CH<sub>3</sub> distances were estimated and that the molecule lay at a crystallographic inversion center and so was rigorously

\* Lists of anisotropic thermal parameters, H-atom positions, structure factors, C—C distances and C—C—C angles within the *p*-tolyl ligands have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54965 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR0014]

square planar. The central Ir(I) atom in the present complex is in a square-planar environment with *trans* tri-*p*-tolylphosphine ligands [Ir—P(1) = 2.305 (3), Ir—P(2) = 2.302 (3) Å {2.300 (1) Å}, P(1)—Ir—P(2) = 175.1 (1)° {180°}]. The Ir—CO bond length is 1.867 (17) Å {1.835 Å} with C(1)—O(1) = 1.122 (22) Å {1.14 Å, assumed}. The Ir—CH<sub>3</sub> distance is 2.206 (13) Å {2.17 Å} and is *trans* to the carbonyl ligand with C(1)—Ir—C(2) = 172.8 (6)° {180°}.

Distances and angles within the *p*-tolyl ligands are normal, with P—C bond lengths ranging from 1.816 (13) through 1.868 (18) Å {1.825 (3)–1.834 (3) Å}, averaging  $1.844 \pm 0.019 \text{ Å}$  { $1.830 \pm 0.005 \text{ Å}$ }. The present complex is isomorphous with *trans*-carbonylchlorobis(tri-*p*-tolylphosphine)iridium-(I) (Churchill, Fettinger, Rappoli & Atwood, 1987).

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## Structure of 1,1-Dioxo-2,4,4,6-tetraphenyl-4*H*-thiopyran Benzene Solvate

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**Abstract.** C<sub>29</sub>H<sub>22</sub>O<sub>2</sub>S<sub>1/2</sub>C<sub>6</sub>H<sub>6</sub>,  $M_r = 473.61$ , monoclinic,  $P2_1/c$ ,  $a = 9.029$  (4),  $b = 13.265$  (4),  $c = 21.426$  (11) Å,  $\beta = 92.62$  (4)°,  $V = 2564$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.227 \text{ g cm}^{-3}$ ,  $\lambda(\text{Cu } K\alpha) = 1.54184 \text{ Å}$ ,  $\mu = 12.95 \text{ cm}^{-1}$ ,  $F(000) = 996$ ,  $T = 294 \text{ K}$ ,  $R = 0.052$  for 3161 unique observed reflections. The central ring

adopts a boat conformation with S1 and C4 displaced by 0.108 (6) and 0.041 (6) Å, respectively, out of the least-squares plane through the remaining ring atoms. The phenyl rings at C2 and C6 make dihedral angles of 58.2 (2) and  $-44.7$  (3)°, respectively, with this least-squares plane. The orientations of the

phenyl rings at C4 are given by the torsion angles, C411—C4—C421—C422 = 4.7 (4) and C421—C4—C411—C416 = 65.2 (3)°. The solvate molecule was found to be disordered and had to be fixed during refinement.

**Experimental.** The title compound was crystallized from heptane–benzene solution (Šebek & Kuthan, 1991). The crystals were colourless in daylight and showed no photochromic effect in the UV region. The samples contained solvent molecules of crystallization, which could not be removed by simple thermostating at 373 K for several hours. The IR and mass spectra were analysed before and after the thermostating. The crystal selected for data collection was a prism 0.6 × 0.4 × 0.4 mm. A set of unique reflections was collected giving 3509 reflections of which 3161 were considered observed [ $I > 1.96\sigma(I)$ ], using a Syntex P2<sub>1</sub> diffractometer with a  $\theta$ – $2\theta$  scan. Cell constants were obtained from 15 reflections with  $17.0 < 2\theta < 29.8^\circ$ . Indices ranged up to  $2\theta_{\max} = 120^\circ$  with  $h$  0/9,  $k$  0/14,  $l$  –23/23. Three standard reflections (040, 200, 015) were measured after each set of 40 reflections without any significant variation. The data were corrected for the Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods using MULTAN87 (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987), which gave the complete molecule of the title compound, but peaks at the solvent site were difficult to interpret. Benzene atoms had to be fixed to the regular hexagon with the centre situated at  $0, \frac{1}{2}, \frac{1}{2}$  during the refinement. The site occupation factors of the benzene C atoms converged close to 0.5 and therefore were fixed at this value in the last steps of the refinement. Originally, the coordinates of H atoms were set according to their ideal distances to the corresponding C atoms and then refined freely. The function minimized in the program SHELX76 (Sheldrick, 1976) was  $\sum[w(|F_o| - |F_c|)^2]$ , where  $w = [\sigma^2(F_o) + 0.0009|F_o|^2]^{-1}$ . The final full-matrix least-squares refinement of 397 parameters, anisotropically for all non-H atoms and isotropically for H atoms (benzene H atoms omitted), converged at  $R = 0.052$ ,  $wR = 0.082$  and  $S = 1.65$ ; the high value of  $wR$  is attributed to the solvent disorder. The highest and the lowest peaks in the final difference electron density map were 0.36 and  $-0.34 \text{ e } \text{Å}^{-3}$ . Maximal shift in the last cycle was smaller than 0.12 e.s.d.'s for all refined parameters, except for the anisotropic thermal parameters of benzene C atoms; their refinement was stopped when shifts fell below 0.4 e.s.d.'s. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Molecular geometry and interatomic distances were calculated by PARST (Nardelli, 1978).

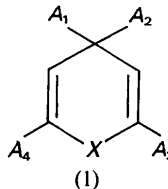
Table 1. Final coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\times 10^3 \text{ Å}^2$ ) with e.s.d.'s in parentheses for the non-H atoms

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

	x	y	z	$U_{\text{eq}}$
C2	2529 (3)	2890 (2)	6218 (1)	41 (1)
C3	1797 (3)	2752 (2)	5679 (1)	43 (1)
C4	1183 (3)	1784 (2)	5391 (1)	41 (1)
C5	1359 (3)	887 (2)	5818 (1)	41 (1)
C6	2002 (2)	826 (2)	6387 (1)	38 (1)
C21	3147 (3)	3883 (2)	6420 (1)	47 (1)
C22	2724 (4)	4359 (2)	6949 (2)	67 (1)
C23	3273 (5)	5320 (2)	7100 (2)	84 (1)
C24	4204 (5)	5792 (3)	6727 (2)	87 (1)
C25	4660 (4)	5325 (3)	6209 (2)	87 (1)
C26	4150 (4)	4363 (2)	6046 (2)	65 (1)
C61	1976 (2)	–94 (2)	6781 (1)	40 (1)
C62	3220 (5)	–439 (3)	7121 (2)	58 (5)
C63	3191 (4)	–1315 (2)	7458 (1)	70 (1)
C64	1901 (3)	–1875 (2)	7466 (1)	68 (1)
C65	648 (4)	–1541 (2)	7134 (1)	64 (1)
C66	682 (3)	–656 (2)	6804 (1)	51 (1)
C411	2004 (2)	1615 (2)	4782 (1)	42 (1)
C412	2744 (3)	734 (2)	4664 (1)	55 (1)
C413	3493 (4)	623 (3)	4108 (2)	70 (1)
C414	3488 (4)	1392 (3)	3682 (2)	73 (1)
C415	2749 (4)	2269 (3)	3797 (1)	64 (1)
C416	2026 (3)	2390 (2)	4339 (1)	54 (2)
C421	–508 (3)	1916 (2)	5272 (1)	43 (1)
C422	–1217 (3)	1816 (2)	4689 (1)	51 (1)
C423	–2757 (3)	1916 (2)	4620 (2)	66 (1)
C424	–3574 (4)	2109 (2)	5115 (2)	75 (1)
C425	–2879 (4)	2211 (3)	5711 (2)	78 (1)
C426	–1372 (3)	2118 (2)	5779 (1)	60 (1)
S1	2927 (1)	1879 (1)	6731 (1)	42 (1)
O1	2287 (3)	2080 (2)	7313 (1)	74 (1)
O2	4499 (2)	1710 (2)	6748 (1)	72 (1)
C7	656 (9)	5422 (9)	5541 (9)	290 (8)
C8	–700 (9)	4923 (9)	5565 (9)	370 (10)
C9	–1356 (9)	4501 (9)	5024 (9)	312 (8)

The fractional coordinates and the equivalent isotropic thermal parameters of all non-H atoms are listed in Table 1. The atomic numbering scheme with thermal ellipsoids for non-H atoms is drawn using ORTEP (Johnson, 1976) in Fig. 1. Interatomic distances and selected angles are listed in Table 2.\*

**Related literature.** A series of compounds with the common molecular scheme (1) is excitable to the photochromic state, in which a new absorption band appears approximately in the range 0.4–0.8  $\mu\text{m}$ .



\* List of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54895 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: L10092]

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

S1—C2	1.762 (3)	S1—C6	1.771 (3)
S1—O1	1.423 (3)	S1—O2	1.436 (2)
C2—C3	1.315 (3)	C2—C21	1.488 (4)
C3—C4	1.518 (4)	C4—C5	1.505 (4)
C4—C411	1.546 (3)	C4—C421	1.546 (4)
C5—C6	1.329 (3)	C6—C61	1.485 (5)
C21—C22	1.367 (5)	C21—C26	1.391 (5)
C22—C23	1.400 (4)	C23—C24	1.341 (6)
C24—C25	1.352 (6)	C25—C26	1.396 (5)
C61—C62	1.389 (5)	C61—C66	1.388 (4)
C62—C63	1.369 (5)	C63—C64	1.382 (4)
C64—C65	1.383 (4)	C65—C66	1.370 (4)
C411—C412	1.375 (4)	C411—C416	1.400 (4)
C412—C413	1.404 (5)	C413—C414	1.369 (6)
C414—C415	1.369 (6)	C415—C416	1.367 (4)
C421—C422	1.384 (4)	C421—C426	1.392 (4)
C422—C423	1.398 (4)	C423—C424	1.344 (6)
C424—C425	1.403 (6)	C425—C426	1.367 (5)
O1—S1—O2	116.6 (2)	C6—S1—O2	109.6 (2)
C6—S1—O1	108.0 (2)	C2—S1—O2	107.9 (2)
C2—S1—O1	109.0 (2)	C2—S1—C6	105.2 (2)
S1—C2—C21	115.4 (2)	S1—C2—C3	121.5 (2)
C2—C3—C4	129.3 (2)	C3—C4—C421	108.1 (2)
C3—C4—C411	106.6 (2)	C3—C4—C5	113.3 (2)
C411—C4—C421	112.6 (2)	C5—C4—C421	105.4 (2)
C5—C4—C411	110.9 (2)	C4—C5—C6	129.5 (3)
S1—C6—C5	120.8 (2)	S1—C6—C61	115.6 (2)
C22—C21—C26	118.7 (3)	C21—C22—C23	120.2 (4)
C21—C26—C25	119.4 (4)	C62—C61—C66	117.8 (3)
C61—C62—C63	121.4 (4)	C61—C66—C65	121.1 (3)
C412—C411—C416	118.5 (2)	C411—C412—C413	120.1 (3)
C411—C416—C415	120.8 (3)	C422—C421—C426	118.1 (3)
C421—C422—C423	120.2 (3)	C421—C426—C425	121.6 (3)

To exclude a strong dependence of the photochromic behaviour on substituents at sites 2, 4 and 6, we have studied the series of equally substituted structures  $A_1 = A_2 = A_3 = A_4 = \text{phenyl}$ :  $X = \text{NH}$  (Iwasaki, Watanabe & Maeda, 1987),  $X = \text{O}$  (Vojtěchovský & Hašek, 1990),  $X = \text{S}$  (Vojtěchovský, Hašek, Nešpůrek & Adamec, 1991),  $X = \text{N—Ph}$  (Vojtěchovský, Hašek, Huml & Ječný, 1990),  $X = \text{NCH}_2\text{C}_5\text{H}_6$  (Hašek & Ondráček, 1990). The title compound ( $X = \text{SO}_2$ ) is not photochromic.

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## Structure of 1-Oxo-2,4,4,6-tetraphenyl-4H-thiopyran Benzene Solvate

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**Abstract.**  $\text{C}_{29}\text{H}_{22}\text{OS}\cdot\frac{1}{4}\text{C}_6\text{H}_6$ ,  $M_r = 439.57$ , triclinic,  $P\bar{1}$ ,  $a = 10.622$  (3),  $b = 11.448$  (2),  $c = 12.343$  (3) Å,  $\alpha = 96.08$  (2),  $\beta = 69.42$  (2),  $\gamma = 67.69$  (2)°,  $V = 1249.3$  (6) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.161$  g cm<sup>-3</sup>,  $\lambda(\text{Cu K}\alpha) = 1.54184$  Å,  $\mu = 12.49$  cm<sup>-1</sup>,  $F(000) = 461$ ,  $T =$

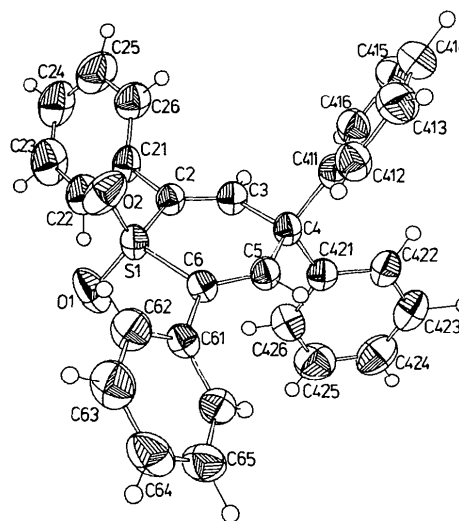


Fig. 1. The atomic numbering scheme with thermal ellipsoids at the 50% probability level.

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