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1,2,3,4-Tetraphenylbutane-1,4-dione benzene solvate and a brief analysis of the solvated organic structures in the Cambridge Structural Database

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1,2,3,4-Tetraphenylbutane-1,4-dione crystallizes as a benzene solvate in a 1:1 ratio, $C_{28}H_{22}O_2 \cdot C_6H_6$. Both molecules reside on crystallographic inversion centers. The carbonyl group of (I) is coplanar with the adjacent phenyl ring within 3.6 (3)°. A brief analysis of the organic structures included in the Cambridge Structural Database [Allen (2002). *Acta Cryst.* B**58**, 380–388] shows that at least 22.8% of them contain cocrystallized solvent and in 3.8% of these cases the solvent is benzene.

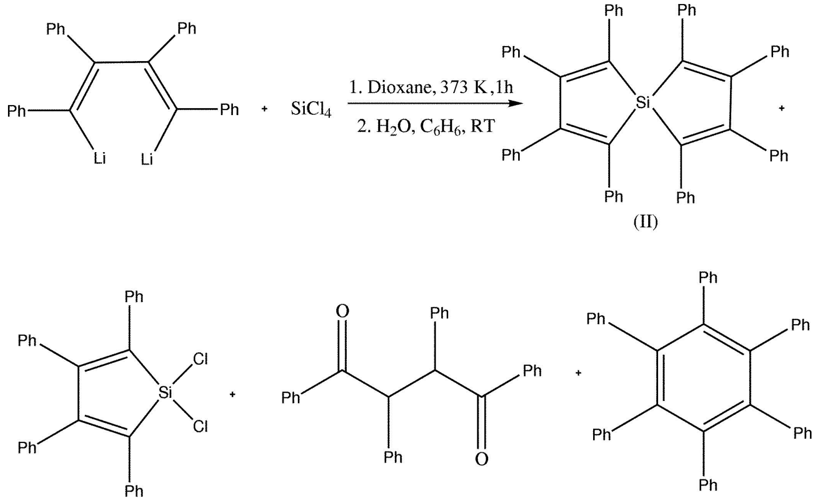
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.054
wR factor = 0.139
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

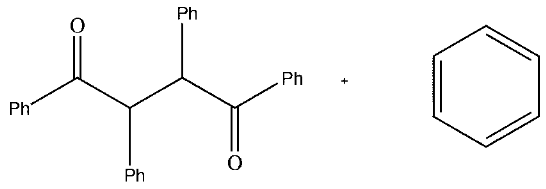
Comment

During the course of our research toward the synthesis of octaphenyl-1,1-spirobisilole (II) and its derivatives, we isolated and spectroscopically and structurally characterized the title compound, (I).



(II)

The Si-containing spiro compound (II) and its derivatives may be used for the construction of long-life white-emitting electroluminiscent devices, displays and electric appliances (Fukuda & Genda, 2004; Matsuura *et al.*, 2003). While compound (II) has not been isolated and characterized,



(I)

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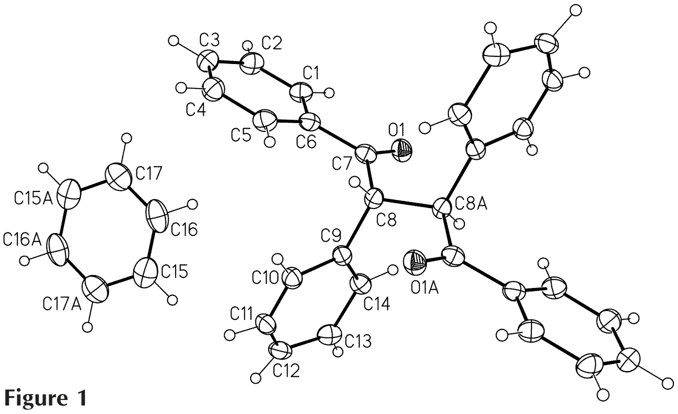

Figure 1

Molecular structure of (1). Displacement ellipsoids are shown at the 50% probability level. The suffixes A denote the symmetry operations ($-x$, $-y + 2$, $-z + 1$) for the 1,2,3,4-tetraphenylbutane-1,4-dione molecule and ($-x + 1$, $-y + 1$, $-z$) for the benzene solvent molecule.

compound (I) was obtained from the reaction between 1,4-dilithiotetraphenylbutadiene and silicon tetrachloride in ~5% yield by apparent incorporation of ambient oxygen or reaction with water. This compound has been isolated and characterized spectroscopically (Amat-Guerri *et al.*, 1990; Ceylan *et al.*, 2004) and our spectra (Timokhin *et al.*, 2005) are consistent with the literature data, but the structural analysis is presented here for the first time.

Compound (I) crystallizes as a benzene solvate in a triclinic unit cell with both molecules occupying crystallographic inversion centers. After the final refinement, several peaks of ~ 0.7 e Å^{-3} were observed in the vicinity of the inversion center occupied by (I). A careful examination of the locations of the peaks indicated a possible second position of the C8–C14 benzyl group, and an alternative refinement accounting for this disorder yielded a ~9:1 ratio for the disordered group. The *R* factor dropped to 0.042, the height of the residual peaks reduced to ~ 0.2 e Å^{-3} and the standard uncertainties for bond distances improved negligibly. However, given the need for an idealized geometry for the minor component, and some resultant C—C distances in excess of 1.6 Å between the minor component, the ordered part of the molecule and the symmetry-related minor component, we decided to ignore the disorder as it is chemically inconsequential. While the disorder is likely to be real, the results of modeling 11% occupied C atoms are not highly reliable.

The overall molecular geometry is normal, the C=O bond distance measuring 1.214 (2) Å and the O1=C7—C6—C1 torsion angle being 3.6 (3)°. In the optimized molecule of (I) at the PBE1PBE/6–31+G* level of theory, the corresponding values are 1.221 Å and 8.83° (Frisch *et al.*, 2004). A search of the Cambridge Structural Database (CSD; Version 5.26, May 2005 update; Allen, 2002) for compounds containing Csp^3—C(=O)—Ph, limited to organic structures with final *R* values of 0.05 or lower, no disorder and no error, and excluding powder structures and polymers, revealed 282 structures with 337 relevant data (Bruno *et al.* 2002). Among these structures, the average C=O bond distance was found to be 1.216 (8) Å, a value in excellent agreement with the C=O bond distance in (I). The range for the above O=C—C—C torsion angle among the 337 data spanned from −54 to 38°. While there are no classical hydrogen bonds present in the structure, the position of the solvent benzene molecule may indicate a weak intermolecular interaction between atom H16 and the C1–C6 phenyl ring. Atom H16 is positioned 3.24 Å from the center of the ring, the C16—H16$\cdots$centroid(C1–C6) angle being 167 (1)°. Since the structure of the title compound contained a benzene solvent molecule, we analyzed the organic structures reported to the CSD for the presence of cocrystallized solvents in the crystal structure. The search revealed 149417 entries for organic molecules, of which at least 34040 (22.8%) are solvated compounds. Benzene is estimated to be the second most frequently observed cocrystallized solvent. The results of our searches for structures with common solvent molecules are presented in Table 1.

Experimental

For the preparation of 1,4-dilithiotetraphenylbutadiene (Hubel *et al.*, 1964; Braye *et al.*, 1961), diphenylacetylene (3.0 g, 16.8 mmol) was shaken with excess of lithium (0.6 g, 86.5 mmol) in diethyl ether (8 ml) under an argon atmosphere. After an induction period of about 10 min, the reaction mixture became brown–red. Shaking was continued for 2 h. The solution of 1,4-dilithiotetraphenylbutadiene in diethyl ether was filtered and used for further reaction. A suspension of 1,4-dilithiotetraphenylbutadiene in diethyl ether was cannulated in a flask with silicon tetrachloride (0.34 ml, 2.97 mmol) in dioxane (60 ml). The ether was removed by distillation. After 1 h of reflux at 373 K, water (10 ml) and benzene (50 ml) were added, and the solvents were removed by distillation. The yellow–green solid was purified by column chromatography (eluent hexanes–benzene, 0→100% benzene). Compound (I) was isolated as colorless crystals from $CDCl_3$ (yield ~5%, based on the starting diphenylacetylene). The ^1H and ^{13}C NMR spectra of (I) in solution are consistent with the structure of the product found in the crystal structure and for the NMR spectral data in the literature (Amat-Guerri *et al.*, 1990; Ceylan *et al.*, 2004). In this reaction, a small amount of hexamethylbenzene was also isolated as pale-yellow crystals from $CDCl_3/CH_2Cl_2$ (yield ~3%, based on the starting diphenylacetylene). The presence of hexamethylbenzene was found by the X-ray crystal analysis.

Crystal data

$C_{28}H_{22}O_2 \cdot C_6H_6$
$M_r = 468.56$
Triclinic, $P\overline{1}$
$a = 8.4629$ (13) Å
$b = 8.7530$ (13) Å
$c = 9.5926$ (14) Å
$\alpha = 110.489$ (2)°
$\beta = 94.886$ (2)°
$\gamma = 108.300$ (2)°
$V = 616.57$ (16) Å^3

$Z = 1$
$D_x = 1.262$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 2387 reflections
$\theta = 2.3$–26.4°
$\mu = 0.08$ mm^{-1}
$T = 100$ (2) K
Needle, colorless
0.47 × 0.40 × 0.30 mm

Data collection

Bruker CCD 1000 area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2003)
$T_{min} = 0.965$, $T_{max} = 0.977$
5010 measured reflections

2468 independent reflections
1972 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 26.4°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.139$
$S = 1.03$
2468 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0528P)^2 + 0.5916P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected common solvents cocrystallized with organic compounds reported to the CSD.

The percentages are reported relative to all organic structures contained in the CSD.

Solvent name	Number of structures	Percentage
Water	11556	7.7
Benzene	5674	3.8
Hexane	2310	1.6
Tetrahydrofuran	2303	1.5
Methanol	2151	1.4
Toluene	1683	1.1
Ethanol	1427	1.0
Dichloromethane	1396	0.9
Chloroform	1163	0.8
Pentane	1086	0.7
Acetonitrile	1057	0.7
Acetone	882	0.6
Diethylether	606	0.4
Dimethylsulfoxide	448	0.3
Propanol	325	0.2

All H atoms were refined using a riding model, with C—H = 0.95 (aromatic) and C—H = 1.00 Å (other H atom), and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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